

Microstructure-resolved and homogenized modeling of porous lithium-ion cathode particles with conductive-additive effects

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Abstract

Li-ion battery performance depends strongly on the microstructure of active material particles, as well as on the surrounding conductive-additive network for enhancing electronic conductivity. The transport processes through the porous structure of common lithium nickel manganese cobalt oxide (NMC) cathode particles are significantly influenced by these morphological aspects which are numerically investigated in this paper. We present two modeling approaches studying the electrochemical behavior of porous particles incorporating conductive-additive effects, within a defined benchmark problem. Alongside a detailed 3D microscopic model as reference, we develop a homogenized multiscale macroscopic model incorporating additive impact. Realistic microstructures of porous NMC particles are generated using a stochastic model that has been calibrated to tomographic image data. Furthermore, a virtual approach is employed to introduce different morphologies of interfacial conductive additives. The 1D implementation of the proposed homogenized model is compared with 3D microstructure-resolved simulations across variations in particle porosity, size, additive coverage, and active-material transport properties during 5C discharge. After calibration of the surface jump closures, the homogenized 1D model closely reproduces the corresponding microstructure-resolved behavior while reducing simulation time from hours to about a minute. The results show that porous particle designs are particularly advantageous for low-diffusivity, high-conductivity active materials as lithiation at internal surfaces improves active-material utilization. However, excessive additive coverage blocks outer intercalation sites and electrolyte pathways, thereby increasing transport limitations. The analysis reveals a particle-scale trade-off between electronic contact, electrolyte accessibility, and active-material volume fraction and provides a tractable route toward multiscale simulations of hierarchically structured cathodes.

Keywords: Lithium-ion battery, porous particle, stochastic 3D model, additive impact, homogenized model

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1. Introduction

1.1. Background and motivation

Lithium-ion batteries (LIBs) are central to modern energy-storage technologies, with applications ranging from consumer electronics to electric vehicles and grid storage [1, 2]. Their performance and longevity are strongly influenced by the electrode microstructure, where charge and ion transport processes occur in a complex multiphase domain [3]. This paper focuses on key factors affecting cathode performance. Common cathode materials often consist of porous particles (PP), i.e., porous agglomerates of primary crystallites. Such porous structures enhance battery performance by improving electrolyte penetration and diffusion pathways, thereby increasing active material (AM) utilization and rate capability [4, 5]. At the electrode level, this results in a hierarchical microstructure spanning multiple length scales [6, 7]. Processing parameters such as sintering temperature and calendaring level can tune the hierarchical structure and thereby influence cell performance, as demonstrated in [7] for $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC111) cathodes. Understanding the interplay between microscopic transport mechanisms and macroscopic battery performance is therefore essential for optimizing electrode design and operation.

Physics-based LIB models span a hierarchy from microstructure-resolved descriptions, which explicitly represent the spatial distribution of the constituent phases, to macroscopic continuum models that retain the dominant electrochemical processes through effective parameters [8, 9]. The Doyle–Fuller–Newman (DFN) model is a widely used computationally efficient framework, but microstructural and conductive-additive effects are represented primarily through effective transport properties and constitutive closures [10]. Standard DFN formulations therefore do not resolve local microstructural heterogeneity. By contrast, microstructure-resolved models can directly incorporate 3D tomographic or reconstructed image data and resolve localized transport limitations, albeit at substantially higher computational cost [8, 9].

The importance of such heterogeneity has been demonstrated in both electrode- and particle-scale studies [11]. Image-based simulations have been shown to capture localized effects relevant to degradation under high-current operation [12], while through-plane and in-plane variations in morphology and particle size strongly affect local concentration and reaction-rate distributions [13, 14]. Experimental and numerical single-particle studies have further clarified transport within secondary particles [15, 16, 17]. At the grain scale, resolved NMC models have addressed intergranular fracture [18], anisotropic diffusion associated with crystallographic orientation [19], and intercalation kinetics within multiphase-field formulations [20], while simplifying electrolyte transport through the pore space. Although these approaches provide detailed local information, their computational cost limits their use in systematic particle-design studies and, especially, in simulations of hierarchically structured electrodes.

Conductive additives introduce a second, coupled microstructural design consideration. They are essential for achieving high-rate capability and enabling thicker LIB

73 electrodes by facilitating both local and electrode-scale electron transport. However,
74 excessive additive loading can increase ionic tortuosity, block intercalation sites,
75 and hinder ionic transport through porous particles, ultimately reducing rate per-
76 formance and energy density [21]. Previous modeling work has represented carbon
77 black and binder as coatings around cathode particles [22], investigated cloud-like,
78 film-like, and contact-localized carbon-binder-domain (CBD) morphologies [23], and
79 incorporated CBD effects into porous-electrode models through modified effective
80 transport properties [24]. Explicitly resolved CBD distributions have also been stud-
81 ied in NMC electrodes [25, 26], including the sensitivity of simulated performance to
82 CBD reconstruction from tomography [27]. Tomography-based simulations further
83 show that dense and nanoporous CBD morphologies create a trade-off between elec-
84 tronic connectivity and electrolyte accessibility in electrodes with non-porous parti-
85 cles [28]. DEM-based workflows provide another route to generate CBD-containing
86 composite electrode structures, accounting for phase-specific agglomerate statistics,
87 mechanical properties, and calendaring pressure [29, 30]. Recent digital workflows
88 also couple such DEM-based microstructures with electrochemical simulations and
89 machine-learning surrogates [31]. These developments motivate a particle-scale de-
90 scription that combines porous secondary-particle transport with explicit informa-
91 tion about conductive-additive contact and pore-mouth accessibility while remaining
92 computationally inexpensive enough for systematic parameter studies.

93 *1.2. Modeling approaches and contributions*

94 In this paper, we derive a homogenized particle-scale model for porous cathode par-
95 ticles by applying asymptotic homogenization to the microstructure-resolved gov-
96 erning equations [32, 33]. The resulting continuum equations are not restricted to
97 spherical particles or isotropic effective tensors. Nevertheless, for spherical secondary
98 particles with approximately isotropic microstructures, the resulting equations can
99 be efficiently solved in one spatial dimension.

100 Asymptotic homogenization has been widely used in hierarchically structured and
101 composite materials [34, 35, 36]. In battery applications, Foster et al. derived
102 an effective mechanical description of porous electrodes including AM and binder
103 swelling and external loading [37]. Electrochemical upscaling has also been devel-
104 oped for electrodes containing non-porous bulk particles [38, 39], and asymptotic
105 homogenization has been used to derive thermal-electrochemical models that retain
106 microstructural anisotropy [40]. Volume-averaging approaches provide an alterna-
107 tive route to continuum descriptions [32]. For porous agglomerates, Lueth et al.
108 derived Newman-type equations with an electrolyte-filled intra-particle pore space
109 [41], while Birkholz and Kamlah developed a 1D model of hierarchically structured
110 cathodes with additional scale-separated transport domains and idealized spherical
111 primary particles [42]. In contrast, the present framework obtains the particle-scale
112 transport tensors from tomography-calibrated microstructures and supplements the
113 derived homogenized equations with closures that account for conductive-additive
114 effects at the secondary-particle surface.

115 For numerical assessment, we use the single-particle benchmark defined in Sec-

tion 2.2, which is inspired by experimental studies of individual bulk and porous particles [15, 16, 43, 44]. The benchmark consists of a secondary particle immersed in a spherical electrolyte domain, with conductive-additive configurations of varying surface coverage prescribed at the particle outer surface. The proposed homogenized model is assessed for porous and non-porous particles under 5C discharge conditions by direct comparison with corresponding 3D microstructure-resolved reference simulations.

The employed digital twins are realizations of the stochastic 3D microstructure model proposed in [45]. The model parameters were estimated from tomographic FIB-SEM image data of porous NMC111 particles [7], and validated with respect to geometric and transport-relevant descriptors to ensure realistic particle morphologies [45]. Moreover, in the present study, this stochastic model has been extended to include a gradient in local volume fractions towards the boundary of the generated particles. Owing to the parametric nature of the model, individual morphology parameters can be systematically varied to generate a large database of virtual porous NMC111 particles with realistically varying structures. Note that this virtual materials testing approach has previously been used in several studies [46, 47, 48, 49].

The present paper makes three main contributions. First, we derive a particle-scale homogenized electrochemical model with effective transport tensors computed from tomography-calibrated porous microstructures. Second, we introduce explicit surface descriptors for electronic contact and electrolyte access and calibrate corresponding jump closures from 3D microstructure-resolved simulations. Third, we benchmark the resulting reduced model across variations in particle porosity, size, additive coverage, and intrinsic AM transport properties. This combined analysis provides insight into the behavior of porous cathode particles and quantifies the competition between electronic contact, electrolyte accessibility, and active-material volume fraction within the investigated single-particle benchmark.

This study is therefore a numerical model-development and benchmarking investigation, with particular emphasis on methodological verification through comparison of the proposed homogenized framework with reference microstructure-resolved simulations. Direct experimental separation of the individual microscale transport contributions and additive-induced surface effects is challenging. Therefore, experimental validation of the resulting particle-scale closure relations remains an important subject for subsequent works.

The remainder of this paper is organized as follows. Section 2 introduces the virtual micro-battery benchmark used to investigate the microscale effects of particle and conductive-additive morphology. Section 3 describes the generation of virtual NMC cathode-particle microstructures and conductive-additive surface configurations. Section 4 presents the microscopic and homogenized electrochemical models, and Section 5 details their numerical implementation. Finally, Section 6 assesses the homogenized model and examines the coupled effects of particle microstructure and additive configuration on particle-scale transport and electrochemical perfor-

159 mance.

160 2. Electrode microstructure and benchmark problem

161 2.1. Hierarchically structured cathode electrodes

162 A LIB with porous AM particles exhibits a hierarchical structure spanning three
 163 characteristic length scales: the electrode, secondary-particle, and primary-particle
 164 scales, as schematically illustrated in Fig. 1a. A key advantage of porous secondary
 165 particles in high-performance applications is the additional internal pore network
 166 and reaction area, which can facilitate electrolyte access and lithiation at internal
 167 AM surfaces.

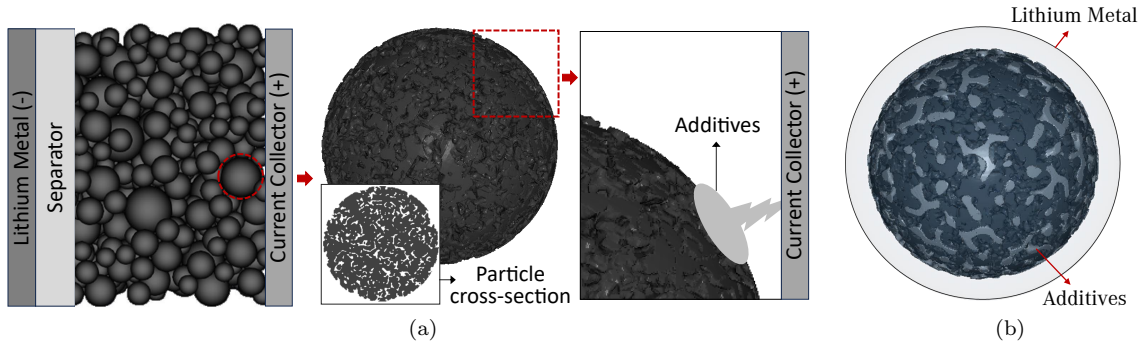


Figure 1: Schematic representation of (a) a hierarchically structured cathode containing porous secondary particles and a conductive-additive network; and (b) the single-particle micro-battery benchmark used in this study, where the voids inside the porous particle and the surrounding shell are filled with liquid electrolyte. The gray region in the secondary particle cross-section indicates the active material domain.

168 At the electrode scale, the conductive-additive network provides electronic pathways
 169 between the current collector and the surfaces of the secondary particles, thereby
 170 compensating for the comparatively low electronic conductivity of the AM. This ben-
 171 efit is accompanied by competing effects because additive-filled regions can increase
 172 electrolyte tortuosity, and surface coverage can partially block accessible intercala-
 173 tion sites and pore openings. The present benchmark isolates these particle-surface
 174 mechanisms. Electrode-level consequences such as inactive-phase loading and full-
 175 cell energy density require an electrode-scale description and are not evaluated di-
 176 rectly here.

177 The objective of the present particle-scale homogenized model is to reproduce the
 178 transport behavior of a porous secondary particle, including additive-induced sur-
 179 face effects, without resolving its internal microstructure during every electrochemi-
 180 cal simulation. At the electrode scale, direct lithium transport between neighboring
 181 secondary particles is considered negligible because of their limited geometric contact
 182 area and the slow timescale of solid-state diffusion [50, 51]. Therefore, the result-
 183 ing porous-particle model can serve as a computationally efficient building block
 184 for future electrode-scale simulations, in which the behavior of individual secondary

particles is coupled to transport through the surrounding electrolyte/additive matrix.

2.2. Single-particle benchmark problem

To isolate the coupled effects of porous-particle morphology and conductive-additive coverage, we use the single-particle benchmark shown in Fig. 1b. A spherical secondary particle with internal porosity is placed concentrically inside a spherical electrolyte domain. This concentric configuration minimizes geometric asymmetry so that differences between investigated cases can be attributed primarily to the AM microstructure and additive distribution. Electrical contact is imposed through conductive additives attached to the outer particle surface, while a 1 μm -thick surrounding shell is filled with liquid electrolyte. During discharge, lithium ions released at the lithium-metal boundary are transported through the electrolyte and intercalate into the cathode particle.

3. Microstructure modeling and generation of virtual cathode particles

3.1. Stochastic 3D microstructure model

In this section, we briefly describe the stochastic 3D model used for generating virtual NMC111 particle microstructures that are considered in this study. First, the porous inner structure of individual secondary particles is modeled by an excursion set of a random field that is simulated on a cuboidal sampling window. Then, in a second step, a spherical cutout is taken from this realization to define a spherical particle. This modeling approach has also been used in [52] to successfully model the morphology of hierarchically structured sodium-ion batteries. Moreover, excursion sets of random fields are a powerful tool for modeling various further functional materials [46, 53, 54, 55, 56].

3.1.1. Excursion set model

The morphology of the inner structure of secondary particles consisting of pores and solid is modeled by an excursion set of a χ^2 -random field. More precisely, let $X_1 = \{X_1(t) : t \in \mathbb{R}^3\}$ and $X_2 = \{X_2(t) : t \in \mathbb{R}^3\}$ be independent and identically distributed Gaussian random fields on $\mathbb{R}^3$. Assume that X_1 and X_2 are motion-invariant, i.e. stationary and isotropic, with $\mathbb{E}X_i(t) = 0$ and $\text{Var } X_i(t) = 1$ for all $t \in \mathbb{R}^3$ and $i \in \{1, 2\}$. The correlation function $\rho_X : \mathbb{R}^3 \times \mathbb{R}^3 \rightarrow (0, 1]$ of X_i , $i = 1, 2$, is chosen as $\rho_X(s, t) = e^{-(mh)^2}$, where $h = \|s - t\|$ for any $s, t \in \mathbb{R}^3$. Note that, due to the isotropy of X_i , $i = 1, 2$, the correlation of the random variables $X_i(s)$ and $X_i(t)$ depends only on the distance $h = \|s - t\|$ between s and t . The value of $m = 4.625 \mu\text{m}^{-1}$, chosen in [45], was estimated based on tomographic image data. For an introduction to Gaussian random fields and their geometric properties, we refer to [57, 58]. Using the random fields X_1 and X_2 , the random variables $Y(t) = X_1^2(t) + X_2^2(t)$, $t \in \mathbb{R}^3$, define the χ^2 -random field $Y = \{Y(t) : t \in \mathbb{R}^3\}$ with two degrees of freedom. For local volume fractions of AM given by some function

224 $\mu: \mathbb{R}^3 \rightarrow (0, 1)$, we now threshold the random field $Y = \{Y(t): t \in \mathbb{R}^3\}$ to obtain
 225 the random excursion set

$$\Xi = \{t \in \mathbb{R}^3: Y(t) \geq \chi_{2,1-\mu(t)}^2\}, \quad (1)$$

226 where $\chi_{2,1-p}^2$ denotes the $1 - p$ quantile of the χ^2 -distribution with two degrees of
 227 freedom for any $p \in (0, 1)$. Note that the function μ directly controls the local
 228 volume fraction of the random set Ξ . Moreover, the distribution of Ξ is uniquely
 229 determined by the functions ρ_X and μ . In [45], parameter versions of ρ_X and μ were
 230 estimated based on tomographic image data, under the assumption of a constant
 231 local volume fraction μ . This was reasonable, as tomographic image data of the inner
 232 structure of the particles considered in [45] did not show drastic variations in the
 233 local volume fraction of AM. Subsequently, the use of realizations of the random set
 234 Ξ as digital twins of the porous inner structure of NMC111 particles was validated
 235 based on various geometric descriptors of Ξ not used for model fitting.

236 In the present paper, we extend the model introduced in [45] by allowing for a varying
 237 local volume fraction $\mu(t)$ of AM. This is needed for a more detailed modeling of the
 238 NMC111 particles, as we observe a certain decrease in the inner particle porosity
 239 in close vicinity of their boundary, see Section 3.1.2 for further details. Finally, in
 240 order to obtain a realization of a spherical particle from a realization of Ξ in a three-
 241 dimensional cube, we simply take a spherical cutout of a given radius, centered at
 242 the origin. Figure 2a shows a 2D slice of a realization of Ξ and of the resulting
 virtually generated particle.

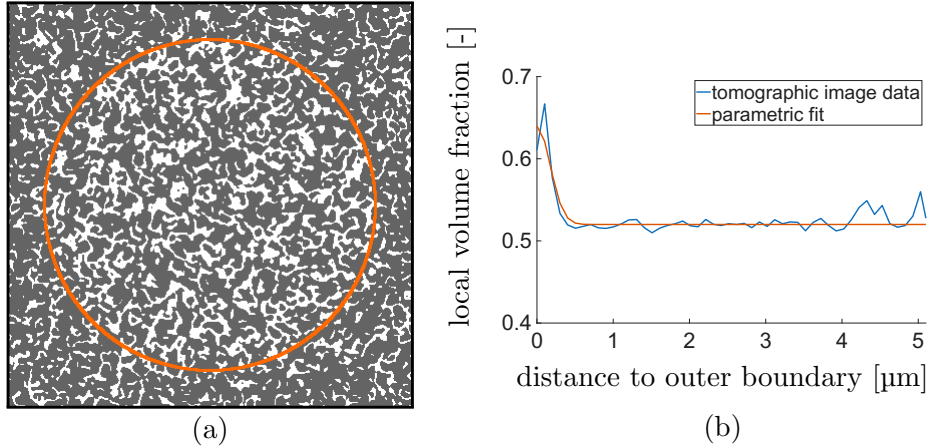


Figure 2: 2D slice of a realization of Ξ in a cube (a), where gray areas correspond to AM and white areas correspond to pore space. The orange circle indicates the spherical cutout used for the realization of the virtual particle. Local volume fraction $\tilde{\mu}_{\alpha,\beta,\gamma,r}(\tilde{h})$ of AM in dependence of the distance $\tilde{h}$ to the outer boundary of porous secondary particles (b), computed for tomographic image data of NMC111 secondary particles (blue) and for samples drawn for the fitted excursion set model (red).

243

3.1.2. Parameter estimation

We assume that the local volume fraction $\mu(t)$ of the random set Ξ given in Eq. (1) is invariant under rotation. That is, the value of $\mu(t)$ at a given point $t \in \mathbb{R}^3$ only depends on the distance $\|t\|$ of t to the origin, which we assume to be the center of the particle. With some abuse of notation, we then write $\mu(t) = \mu(h)$, for any $t \in \mathbb{R}^3$ such that $h = \|t\|$. We consider a parametric fit for the function $\mu : [0, \infty) \rightarrow (0, 1]$ of the form

$$\mu_{\alpha,\beta,\gamma,r}(h) = \min \{ \alpha e^{-\beta \max\{r-h,0\}^2} + \gamma, 1 \}, \quad (2)$$

for any $h \geq 0$ and some parameters $\alpha, \beta, r > 0$ and $\gamma \in (0, 1)$. The parameter $r > 0$ models the radius of the resulting virtual secondary particle. Note that the value of r is identical with the value the radius used to determine the particle boundary in Section 3.1.1. With this choice of the function of the local volume fraction of AM, the prescribed expected volume fraction of the excursion set Ξ is approximately equal to γ in the interior of the particles, and equal to $\min\{\alpha + \gamma, 1\}$ at their boundary. The maximum in Eq. (2) ensures that the volume fraction remains at $\alpha + \gamma$ outside the sphere with radius r . The parameter β controls the rate at which the volume fraction changes when approaching the boundary. The minimum in Eq. (2) ensures that $\mu_{\alpha,\beta,\gamma,r}(h)$ does not take unrealistic values above 1.

Figure 2b shows the fit of the function $\tilde{\mu}_{\alpha,\beta,\gamma,r} : [0, r] \rightarrow (0, 1]$, where $\tilde{\mu}_{\alpha,\beta,\gamma,r}(\tilde{h}) = \mu_{\alpha,\beta,\gamma,r}(r - \tilde{h})$ for each $\tilde{h} \in [0, r]$, to the local volume fractions of AM in NMC111 particles, which have been estimated based on tomographic image data. The radius $r = 5.5 \mu\text{m}$ has been estimated in the same way, while the values of $\alpha = 0.12$, $\beta = 16.8 \mu\text{m}^{-2}$ and $\gamma = 0.52$ were determined by means of a least square fit to the estimated function of local volume fractions. For different realizations of virtual particles considered in this study, we keep the parameters α and β fixed based on this estimation, and only vary the parameters r and γ , to obtain digital twins of porous particles with varying radii and volume fractions of AM, see Table 1.

3.2. Database of virtual cathode particles

The values of the parameters γ and r used to generate the different porous particles considered in this study are listed in Table 1. The particles are designated using the notation Pxy , where x identifies the approximate central AM volume fraction through γ , and $y \in \{s, l\}$ denotes the particle size: s (small) for an outer radius of $4.4 \mu\text{m}$ and l (large) for an outer radius of $8.8 \mu\text{m}$. For each particle size, two porous internal structures are generated using the stochastic model described in Section 3.1. For each radius, a third case is also considered, denoted by P100s and P100l, where the internal pores are closed using the morphological closing operation implemented in Simpleware ScanIP (Synopsys, Mountain View, CA, USA), defined as dilation followed by erosion with the same structuring element [59, 60]. These P100 cases serve as pore-closed numerical references under the same intrinsic material properties. In the following, the term “bulk” is used only as shorthand for these pore-closed reference particles. Therefore, in this study, six different virtual cathode particles are considered as depicted in Fig. 3.

Name	γ	r [μm]
P68s	0.68	4.4
P85s	0.85	4.4
P68l	0.68	8.8
P85l	0.85	8.8

Table 1: Parameter values of γ and r used to generate the different porous particles.

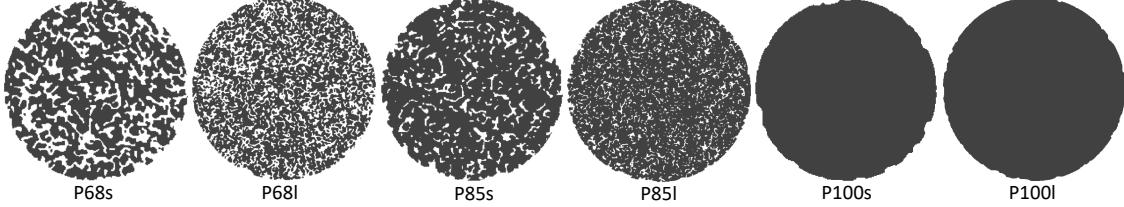


Figure 3: Planar cross-sections of the virtual cathode particles considered in this study.

285 To construct the simulation domains of the single-particle benchmark described in
286 Section 2.2, the generated image stacks with 40 nm voxel size are imported into
287 Simpleware ScanIP. The gray voxels in the image data are assigned to AM and
288 white voxels are assigned to the liquid electrolyte phase.

289 3.3. Morphology and effect of conductive additives

290 In this section, we describe how the spatial distribution of conductive additives at the
291 particle surface influences the effective electrochemical behavior of the reconstructed
292 particles.

293 3.3.1. Spatial distribution of additives at the particle surface

294 To investigate conductive-additive effects, we generate virtual additive distributions
295 with varying surface coverages. Motivated by the limited penetration of the additive
296 phase into the particle pores, a concentric spherical shell with a thickness of $0.2\mu\text{m}$
297 is positioned such that its mid-surface coincides with the outer surface of the sec-
298 ondary particle, as illustrated in Fig. 4a. The prescribed fraction of this shell is then
299 filled using the Neovius surface-lattice generator in Simpleware ScanIP, producing
300 approximately homogeneous additive distributions [59, 61].

301 Eight conductive-additive configurations are considered for each simulated cathode
302 particle, with nominal surface-shell coverages from 5% to 95%. Figure 4b illustrates
303 the additive domain Ω_a generated for a P68s particle, where the AM phase is denoted
304 by Ω_s , and $\Omega_{e,pp}$ denotes the electrolyte-filled pores inside the particle. The notation
305 Ax indicates that $x\%$ of the surface shell is filled with conductive additive. In the
306 idealized Sx variants, additive regions covering pore openings are removed while the
307 AM/additive electronic contacts are retained, providing a controlled comparison of
308 electrolyte-access effects.

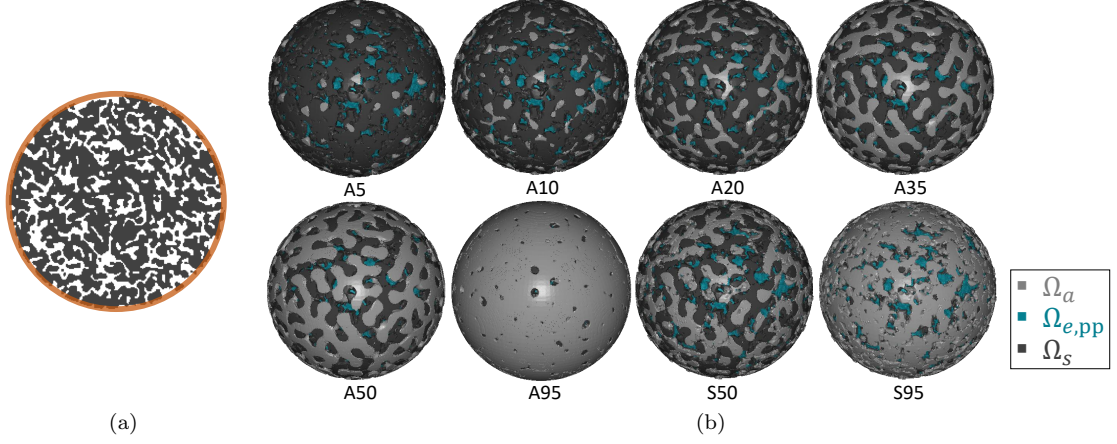


Figure 4: Virtual conductive-additive distributions. (a) Concentric surface shell (brown) used to generate the additive phase. (b) Eight different conductive-additive configurations, demonstrated for a P68s particle, where the additive domain Ω_a is shown in gray, the AM phase Ω_s is shown in black, and the intra-particle electrolyte $\Omega_{e,pp}$ is shown in blue color. Compared to A50 and A95, the S50 and S95 configurations remove additive material that covers pore openings, thereby opening electrolyte pathways to the inner pore, visible through the exposed blue electrolyte domain $\Omega_{e,pp}$.

3.3.2. Effect of conductive additives on transport processes

Figure 5 summarizes the two additive effects represented in the benchmark. The electrolyte domain is decomposed into the intra-particle pore phase, $\Omega_{e,pp}$, and the surrounding electrolyte shell, $\Omega_{e,sh}$. Conductive-additive regions in contact with the AM form type-1 contacts, which provide electronic access, whereas additive regions covering pore openings form type-2 contacts, which obstruct ionic mass and charge transport through the electrolyte phase. Although both contact types occur simultaneously, we additionally consider the idealized S50 and S95 configurations, in which the type-1 contacts are retained while the corresponding type-2 blockages are removed.

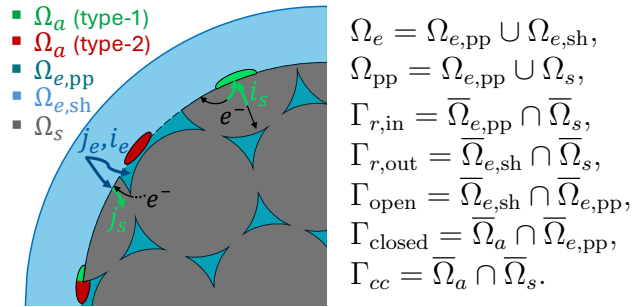


Figure 5: Schematic illustration of conductive additive effects on charge and mass transport processes in porous particles (PP), together with the domain and interface notation used in this study. The type-1 contacts provide electronic connection, whereas type-2 contacts block available electrolyte pathways for charge and mass transport.

The phase domains are taken to be mutually disjoint open sets. Interfaces are therefore defined by intersections of the closures of adjacent phases. Equivalently, for the

present disjoint phases, they coincide with the corresponding boundary intersections. The notations used for the relevant domains and interfaces are summarized in Fig. 5, where $\overline{B}$ denotes the closure of a phase domain $B \subset \mathbb{R}^3$.

Based on these domains and interfaces, we define the geometric quantities used to describe the transport processes. In the following, $|\cdot|$ denotes the volume measure for domains and the surface measure for boundaries and interfaces. The volume fractions of AM and electrolyte inside the porous secondary particle are then defined as

$$\varepsilon_{s,pp} = \frac{|\Omega_s|}{|\Omega_{pp}|}, \quad \varepsilon_{e,pp} = \frac{|\Omega_{e,pp}|}{|\Omega_{pp}|}.$$

The specific surface area of the internal reaction interface, measured with respect to the total volume of the secondary particle, is given by

$$a_{pp} = \frac{|\Gamma_{r,in}|}{|\Omega_{pp}|}.$$

On the outer particle surface, the ratio

$$s_{r,out} = \frac{|\Gamma_{r,out}|}{|\partial\Omega_{pp}|}$$

denotes the fraction of outer intercalation reaction sites. Similarly,

$$s_{open} = \frac{|\Gamma_{open}|}{|\partial\Omega_{pp}|}, \quad s_{cc} = \frac{|\Gamma_{cc}|}{|\partial\Omega_{pp}|}$$

denote the fractions of open electrolyte channels and electrical contacts, respectively. The remaining fraction of the outer particle surface is denoted by

$$s_{closed} = \frac{|\Gamma_{closed}|}{|\partial\Omega_{pp}|}.$$

Thus, the surface fractions for each particle satisfy

$$s_{r,out} + s_{open} + s_{cc} + s_{closed} = 1.$$

The surface coverage ratios obtained from the generated image data for all examined particles and additive distributions are reported in Fig. 6. The error bars indicate the standard deviation of each ratio across the different particle realizations considered in this paper.

4. Electrochemical modeling

4.1. Microstructure-resolved model

This section states the microstructure-resolved electrochemical model that serves as the starting point for homogenization [10]. At time $t > 0$ and microscale position

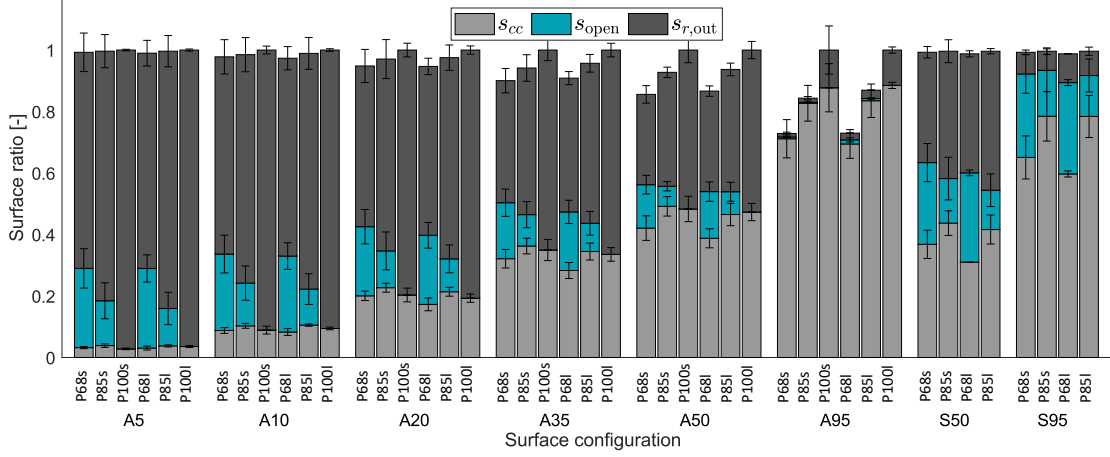


Figure 6: Surface fractions for the investigated particle types and conductive-additive configurations. Error bars show the standard deviation across realizations of a given particle type.

344 x , Eqs. (3)–(6) govern the lithium concentrations $\hat{c}_s$ and $\hat{c}_e$ and electric potentials
 345 $\hat{\phi}_s$ and $\hat{\phi}_e$ in the AM and electrolyte phases, respectively. The material parameters
 346 used in the simulations are summarized in Table 2.

$$347 \quad \partial_t \hat{c}_s(x, t) + \nabla \cdot \hat{j}_s(x, t) = 0, \quad \hat{j}_s(x, t) = -D_s(\hat{c}_s) \nabla \hat{c}_s(x, t), \quad \text{in } \Omega_s, \quad (3)$$

$$348 \quad \nabla \cdot \hat{i}_s(x, t) = 0, \quad \hat{i}_s(x, t) = -\sigma_s(\hat{c}_s) \nabla \hat{\phi}_s(x, t), \quad \text{in } \Omega_s, \quad (4)$$

$$349 \quad \partial_t \hat{c}_e(x, t) + \nabla \cdot \hat{j}_e(x, t) = 0, \quad \hat{j}_e(x, t) = k_{c_1}(\hat{c}_e) \nabla \hat{c}_e(x, t) + k_{c_2}(\hat{c}_e) \nabla \hat{\phi}_e(x, t), \quad \text{in } \Omega_e, \quad (5)$$

$$\nabla \cdot \hat{i}_e(x, t) = 0, \quad \hat{i}_e(x, t) = k_{\phi_1}(\hat{c}_e) \nabla \hat{c}_e(x, t) + k_{\phi_2}(\hat{c}_e) \nabla \hat{\phi}_e(x, t), \quad \text{in } \Omega_e. \quad (6)$$

350 Here, $\hat{j}_s$ and $\hat{j}_e$ denote molar lithium fluxes in the AM and electrolyte phases, re-
 351 spectively, while $\hat{i}_s$ and $\hat{i}_e$ denote the corresponding electric current densities. Fur-
 352 thermore, for the material-dependent coefficients in Eqs. (5) and (6) we have

$$353 \quad k_{c_1}(\hat{c}_e) = -D_e - \frac{2\sigma_e RT t_+^0}{F^2} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) (t_+^0 - 1) \frac{1}{\hat{c}_e(x, t)}, \quad k_{c_2}(\hat{c}_e) = -\frac{\sigma_e t_+^0}{F}, \quad (7)$$

$$k_{\phi_1}(\hat{c}_e) = -\frac{2\sigma_e RT}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) (t_+^0 - 1) \frac{1}{\hat{c}_e(x, t)}, \quad k_{\phi_2}(\hat{c}_e) = -\sigma_e, \quad (8)$$

354 where T is the cell temperature, F is the Faraday's constant, and R is the universal
 355 gas constant.

356 On the AM/electrolyte interface

$$\Gamma_{se} = \overline{\Omega}_s \cap \overline{\Omega}_e,$$

357 where intercalation occurs, mass and charge conservation give

$$-n_s \cdot \hat{j}_s(x, t) = -\hat{j}_r(x, t), \quad -n_s \cdot \hat{i}_s(x, t) = -F \hat{j}_r(x, t), \quad \text{on } \Gamma_{se}, \quad (9)$$

358 and

$$-n_e \cdot \hat{j}_e(x, t) = \hat{j}_r(x, t), \quad -n_e \cdot \hat{i}_e(x, t) = F\hat{j}_r(x, t), \quad \text{on } \Gamma_{se}. \quad (10)$$

359 Here, n_s and n_e denote the outward unit normals of Ω_s and Ω_e , respectively, such
360 that

$$n_e = -n_s, \quad \text{on } \Gamma_{se}.$$

361 The interfacial molar reaction flux $\hat{j}_r$ is evaluated using the Butler–Volmer rela-
362 tion

$$\hat{j}_r(x, t) = \frac{\hat{i}_0(x, t)}{F} \left(e^{\frac{\alpha_a F}{RT} \hat{\eta}(x, t)} - e^{-\frac{\alpha_c F}{RT} \hat{\eta}(x, t)} \right), \quad \text{on } \Gamma_{se}, \quad (11)$$

363 Here, $\hat{i}_0$ is the exchange current density and $\hat{\eta}$ denotes the surface overpotential,
364 given by

$$\hat{i}_0(x, t) = k_0 \left(\frac{\hat{c}_e(x, t)}{c_{e, \text{ref}}} \right)^{\alpha_a} \left(\frac{c_{s, \text{max}} - \hat{c}_s(x, t)}{c_{s, \text{ref}}} \right)^{\alpha_a} \left(\frac{\hat{c}_s(x, t)}{c_{s, \text{ref}}} \right)^{\alpha_c}, \quad \text{on } \Gamma_{se}, \quad (12)$$

365 and

$$\hat{\eta}(x, t) = \hat{\phi}_s(x, t) - \hat{\phi}_e(x, t) - \hat{U}_0(\hat{c}_s(x, t)), \quad \text{on } \Gamma_{se}. \quad (13)$$

366 The reference concentrations $c_{e, \text{ref}}$ and $c_{s, \text{ref}}$ in Eq. (12) are respectively defined as
367 $c_{e, 0}$ and $c_{s, \text{max}}/2$, while $\hat{U}_0$ in Eq. (13) represents the AM equilibrium potential.

368 A zero-Neumann boundary condition is imposed on the non-reactive electrolyte/additive
369 interface Γ_{closed} . The additive phase is represented geometrically and no electronic
370 transport equation is solved inside Ω_a . All AM/additive contact patches are treated
371 as ideally connected to the external electronic reservoir, and the applied current is
372 distributed uniformly over Γ_{cc} . Contact resistance and ohmic or percolation losses
373 inside the additive network are therefore outside the present benchmark. On the
374 AM/additive contact interface Γ_{cc} , where the applied current $I_{\text{app}}(t)$ is imposed¹,
375 we have

$$-n_s \cdot \hat{j}_s(x, t) = 0, \quad -n_s \cdot \hat{i}_s(x, t) = -\frac{I_{\text{app}}(t)}{|\Gamma_{cc}|}, \quad \text{on } \Gamma_{cc}. \quad (14)$$

376 Furthermore, the boundary conditions on the lithium-metal interface Γ_{Li} read

$$-n_e \cdot \hat{j}_e(x, t) = \hat{j}_{r, \text{Li}}(x, t), \quad -n_e \cdot \hat{i}_e(x, t) = F\hat{j}_{r, \text{Li}}(x, t), \quad \text{on } \Gamma_{\text{Li}}. \quad (15)$$

377 Assuming zero reference potential on the lithium-metal interface, the local overpo-
378 tential equals $-\hat{\phi}_e$, which according to the Butler–Volmer relation leads to

$$\hat{j}_{r, \text{Li}}(x, t) = \frac{k_{0, \text{Li}}}{F} \left(\frac{\hat{c}_e(x, t)}{c_{e, \text{ref}}} \right)^{\alpha_a} \left(e^{-\frac{\alpha_a F}{RT} \hat{\phi}_e(x, t)} - e^{\frac{\alpha_c F}{RT} \hat{\phi}_e(x, t)} \right), \quad \text{on } \Gamma_{\text{Li}}. \quad (16)$$

¹The applied current I_{app} is positive during cell discharge.

379 The simulations are performed at a fixed temperature of $T = 293.15$ K with initial
 380 concentrations

$$\hat{c}_s(x, 0) = c_{s,0} \quad \text{in } \Omega_s, \quad \hat{c}_e(x, 0) = c_{e,0} \quad \text{in } \Omega_e.$$

Parameter	Symbol	Unit	Value
Cathode diffusion coefficient	D_s	m^2/s	according to Table 3
Cathode conductivity	σ_s	S/m	according to Table 3
Cathode maximum lithium concentration	$c_{s,\max}$	mol/m^3	5.0×10^4
Cathode minimum lithium concentration	$c_{s,\min}$	mol/m^3	7.0×10^3
Cathode initial lithium concentration	$c_{s,0}$	mol/m^3	1.1×10^4
Cathodic charge-transfer coefficient	α_c	-	0.5
Anodic charge-transfer coefficient	α_a	-	0.5
Cathode exchange current density	k_0	A/m^2	0.75
Anode exchange current density	$k_{0,\text{Li}}$	A/m^2	100
Electrolyte initial lithium concentration	$c_{e,0}$	mol/m^3	1000
Electrolyte diffusion coefficient	D_e	m^2/s	1.43×10^{-10}
Electrolyte conductivity	σ_e	S/m	0.89
Electrolyte transference number	t_+^0	-	0.46
Electrolyte activity dependence coefficient	$\frac{\partial \ln f_{\pm}}{\partial \ln c_e}$	-	3.47

Table 2: Reference material-related properties.

381 It should be noted that the governing microscopic transport equations within the
 382 active-material particles can be written in the general form

$$\alpha_t \frac{\partial u}{\partial t}(x, t) + \nabla \cdot q(x, t) = 0, \quad q(x, t) = -a(u) \nabla u(x, t), \quad \text{in } \Omega_{\square}, \quad (17)$$

383 supplemented by the Neumann-type interface condition

$$-n \cdot a(u) \nabla u(x, t) = g(x, t).$$

384 A formally similar representation can be used for transport in the electrolyte. How-
 385 ever, the electrolyte equations contain additional coupling terms between the con-
 386 centration and potential fields, which can be treated analogously as explained in the
 387 Appendix A.

388 4.2. Homogenization framework

389 The homogenization framework is based on formal asymptotic expansion in porous
 390 media [32, 33]. We consider a periodically two-phase reference microstructure, as
 391 illustrated schematically in Fig. 7, with the scale ratio $\varepsilon = l/L$. Here, L is the
 392 characteristic size of the secondary-particle domain and l is the characteristic mi-
 393 crostructural length. To derive the macroscopic equations, we study the asymptotic
 394 behavior of the microscopic equations as $\varepsilon \rightarrow 0$ using periodic homogenization on

representative local microstructures. The generated stochastic particles themselves are not periodic. Periodicity is introduced only at the level of the cell problems by periodizing sampled subvolumes used to compute the effective transport tensors, as discussed in Section 5.2.

The accuracy of the homogenized model is assessed by comparison with the 3D microstructure-resolved simulations in Sections 6.1 and 6.3. Related questions concerning the validity of homogenized descriptions at finite scale are discussed in [51].

Since conductive additives penetrate only to a limited extent into the pore space of the active-material phase [3, 21, 62], the internal interface between the two phases in the homogenization problem, denoted by Γ^ε , is identified with the AM/electrolyte intercalation interface inside the secondary particle. Effects of conductive additives at the outer boundary of the secondary particle, $\partial\Omega$, are treated separately through the effective interface conditions introduced in Section 4.3.

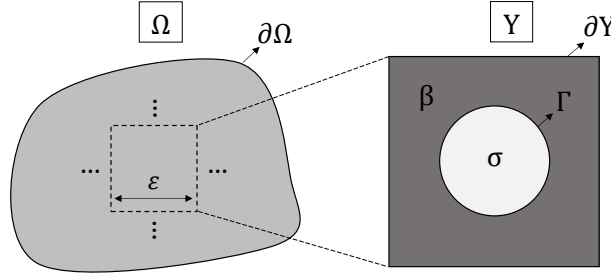


Figure 7: Schematic illustration of the microscale periodic domain Ω for a secondary particle and its corresponding periodic cell Y .

The homogenized form of the generic boundary value problem given in Eq. (17) with Neumann boundary conditions, as described in Appendix A, becomes

$$\alpha_t \frac{|\beta|}{|Y|} \frac{\partial u_0}{\partial t}(x, t) + \nabla \cdot q(x, t) + \frac{|\Gamma|}{|Y|} g(x, t) = 0, \quad q(x, t) = -A(u_0) \nabla u_0(x, t), \quad \text{in } \Omega, \quad (18)$$

where $A(u_0) = (a_{i,j})_{i,j}$ denotes the macroscopic property tensor of the underlying periodic microstructure. Within the asymptotic homogenization framework, the internal particle structure determines the effective macroscopic properties, while the outer boundary conditions are imposed directly at the homogenized level.

The macroscopic tensor $A(u_0)$ is given by Eq. (A.16), and only needs to be computed once for each phase using the auxiliary cell problem described in Appendix A, provided that the microstructure remains unchanged. The numerical approach for computing the property tensors is described in Section 5.2.

4.3. Homogenized porous-particle model

The homogenized model uses separate continuum descriptions inside the porous secondary particle and in the surrounding electrolyte shell, coupled at the particle-shell interface. The same domain partitioning is also employed in the post-processing of

the reference microscopic simulations. For notational brevity, hereafter the function arguments are omitted. Applying the upscaling procedure described in Section 4.2 to Eqs. (3)–(6) within the porous particle domain Ω_{pp} , we obtain

$$\varepsilon_{s,\text{pp}} \partial_t c_{s,\text{pp}} + \nabla \cdot j_{s,\text{pp}} + a_{\text{pp}} j_{r,\text{pp}} = 0, \quad j_{s,\text{pp}} = -D_{s,\text{pp}} \nabla c_{s,\text{pp}}, \quad \text{in } \Omega_{\text{pp}}, \quad (19)$$

$$\nabla \cdot i_{s,\text{pp}} + a_{\text{pp}} F j_{r,\text{pp}} = 0, \quad i_{s,\text{pp}} = -\sigma_{s,\text{pp}} \nabla \phi_{s,\text{pp}}, \quad \text{in } \Omega_{\text{pp}}, \quad (20)$$

$$\varepsilon_{e,\text{pp}} \partial_t c_{e,\text{pp}} + \nabla \cdot j_{e,\text{pp}} - a_{\text{pp}} j_{r,\text{pp}} = 0, \quad j_{e,\text{pp}} = k_{c1,\text{pp}} \nabla c_{e,\text{pp}} + k_{c2,\text{pp}} \nabla \phi_{e,\text{pp}}, \quad \text{in } \Omega_{\text{pp}}, \quad (21)$$

$$\nabla \cdot i_{e,\text{pp}} - a_{\text{pp}} F j_{r,\text{pp}} = 0, \quad i_{e,\text{pp}} = k_{\phi1,\text{pp}} \nabla c_{e,\text{pp}} + k_{\phi2,\text{pp}} \nabla \phi_{e,\text{pp}}, \quad \text{in } \Omega_{\text{pp}}. \quad (22)$$

In Eqs. (19)–(22), $D_{s,\text{pp}}$, $\sigma_{s,\text{pp}}$, $k_{c1,\text{pp}}$, $k_{c2,\text{pp}}$, $k_{\phi1,\text{pp}}$ and $k_{\phi2,\text{pp}}$ are the homogenized transport tensors associated with the corresponding microscopic coefficients. The volumetric source terms of the homogenized equations are proportional to the molar reaction flux on internal AM/electrolyte reaction interface, described as

$$j_{r,\text{pp}} = \frac{i_{0,\text{pp}}}{F} \left(e^{\frac{\alpha_a F}{RT} \eta_{\text{pp}}} - e^{-\frac{\alpha_c F}{RT} \eta_{\text{pp}}} \right), \quad \text{in } \Omega_{\text{pp}}, \quad (23)$$

where $i_{0,\text{pp}}$ and η_{pp} denote the intra-particle exchange current density and overpotential, respectively given by

$$i_{0,\text{pp}} = k_0 \left(\frac{c_{e,\text{pp}}}{c_{e,\text{ref}}} \right)^{\alpha_a} \left(\frac{c_{s,\text{max}} - c_{s,\text{pp}}}{c_{s,\text{ref}}} \right)^{\alpha_a} \left(\frac{c_{s,\text{pp}}}{c_{s,\text{ref}}} \right)^{\alpha_c}, \quad \text{in } \Omega_{\text{pp}}, \quad (24)$$

$$\eta_{\text{pp}} = \phi_{s,\text{pp}} - \phi_{e,\text{pp}} - U_0(c_{s,\text{pp}}), \quad \text{in } \Omega_{\text{pp}}. \quad (25)$$

Because no intercalation reaction occurs in the surrounding electrolyte shell Ω_{sh} , Eqs. (5) and (6) reduce to

$$\varepsilon_{e,\text{sh}} \partial_t c_{e,\text{sh}} + \nabla \cdot j_{e,\text{sh}} = 0, \quad j_{e,\text{sh}} = k_{c1,\text{sh}} \nabla c_{e,\text{sh}} + k_{c2,\text{sh}} \nabla \phi_{e,\text{sh}}, \quad \text{in } \Omega_{\text{sh}}, \quad (26)$$

$$\nabla \cdot i_{e,\text{sh}} = 0, \quad i_{e,\text{sh}} = k_{\phi1,\text{sh}} \nabla c_{e,\text{sh}} + k_{\phi2,\text{sh}} \nabla \phi_{e,\text{sh}}, \quad \text{in } \Omega_{\text{sh}}, \quad (27)$$

where $k_{c1,\text{sh}}$, $k_{c2,\text{sh}}$, $k_{\phi1,\text{sh}}$ and $k_{\phi2,\text{sh}}$ are the corresponding transport tensors in the electrolyte shell.

The homogenized transport equations derived in this section are valid in general spatial dimensions. For the present benchmark, the nearly isotropic AM microstructures and the spherical particle geometry motivate an angularly averaged description of the outer interface. The microscopic boundary conditions introduced in Section 4.1 are therefore replaced by surface-averaged conditions on $\partial\Omega_{\text{pp}}$ that preserve the corresponding total fluxes [38, 39].

Let n_{pp} denote the outward normal of Ω_{pp} , pointing to Ω_{sh} . For solid-phase lithium flux, only the outer reaction sites $\Gamma_{r,\text{out}}$ and the electronic contact surface Γ_{cc} are relevant, while the open and closed pore-mouth surfaces, Γ_{open} and Γ_{closed} , belong

449 to the electrolyte-side transport problem. Consequently, the surface-averaged solid-
 450 phase lithium flux across $\partial\Omega_{\text{pp}}$ can be computed as

$$-n_{\text{pp}} \cdot j_{s,\text{pp}} = \frac{1}{|\partial\Omega_{\text{pp}}|} \left(\int_{\Gamma_{r,\text{out}}} -n_{\text{pp}} \cdot j_{s,\text{pp}} ds + \int_{\Gamma_{cc}} -n_{\text{pp}} \cdot j_{s,\text{pp}} ds \right). \quad (28)$$

451 On $\Gamma_{r,\text{out}}$, the solid-phase lithium flux is determined by the outer intercalation re-
 452 action, whereas on Γ_{cc} no lithium is exchanged through the AM/additive contact.
 453 Thus, we obtain

$$-n_{\text{pp}} \cdot j_{s,\text{pp}} = -s_{r,\text{out}} j_{r,\text{out}}, \quad \text{on } \partial\Omega_{\text{pp}}. \quad (29)$$

454 The effective outer-surface reaction flux $j_{r,\text{out}}$ is evaluated with the Butler–Volmer
 455 relation in Eq. (11), using the homogenized interface concentrations and potentials,
 456 and the overpotential

$$\eta_{r,\text{out}} = \phi_{s,\text{pp}} - \phi_{e,\text{sh}} - U_0(c_{s,\text{pp}}), \quad \text{on } \partial\Omega_{\text{pp}}. \quad (30)$$

457 The same surface-averaging argument as in Eq. (28) is used to derive the effective
 458 interface condition for the solid-phase charge transport equation. In this case, the
 459 outer reaction sites on $\Gamma_{r,\text{out}}$ contribute through the Faradaic current, whereas the
 460 applied current is imposed through the Γ_{cc} contact surface, leading to

$$-n_{\text{pp}} \cdot i_{s,\text{pp}} = -s_{r,\text{out}} F j_{r,\text{out}} - i_{\text{app}}, \quad \text{on } \partial\Omega_{\text{pp}}, \quad (31)$$

461 where $i_{\text{app}} = I_{\text{app}}/|\partial\Omega_{\text{pp}}|$ denotes the applied current flux averaged over $\partial\Omega_{\text{pp}}$.

462 To preserve mass and charge conservation and to consistently define the particle–
 463 shell interface conditions, the coupling between the governing equations is examined.
 464 Summing the solid- and electrolyte-phase lithium balances in Eqs. (19) and (21)
 465 eliminates the reaction terms, yielding the local total-lithium balance

$$\partial_t (\varepsilon_{s,\text{pp}} c_{s,\text{pp}} + \varepsilon_{e,\text{pp}} c_{e,\text{pp}}) + \nabla \cdot (j_{s,\text{pp}} + j_{e,\text{pp}}) = 0, \quad \text{in } \Omega_{\text{pp}}. \quad (32)$$

466 Equation (32) shows that interfacial reactions do not create or consume lithium
 467 inside the homogenized particle. They only transfer lithium between the electrolyte
 468 and AM phases. Integrating Eq. (32) over Ω_{pp} yields

$$\frac{d}{dt} \int_{\Omega_{\text{pp}}} (\varepsilon_{s,\text{pp}} c_{s,\text{pp}} + \varepsilon_{e,\text{pp}} c_{e,\text{pp}}) dx + \int_{\partial\Omega_{\text{pp}}} n_{\text{pp}} \cdot (j_{s,\text{pp}} + j_{e,\text{pp}}) ds = 0. \quad (33)$$

469 Thus, the total lithium content of the homogenized porous particle changes only due
 470 to the net flux across $\partial\Omega_{\text{pp}}$. This observation is used to define the conservation of
 471 lithium at the particle–shell interface, which requires the lithium flux entering the
 472 shell to equal the total flux leaving the homogenized particle. Therefore,

$$-n_{\text{sh}} \cdot j_{e,\text{sh}} = \frac{1}{|\partial\Omega_{\text{pp}}|} \int_{\partial\Omega_{\text{pp}}} n_{\text{pp}} \cdot (j_{s,\text{pp}} + j_{e,\text{pp}}) ds. \quad (34)$$

473 The homogenized electrolyte flux $j_{e,pp}$ is a superficial flux defined per total macro-
 474 scopic particle area. Using Eq. (29), the effective shell-side coupling condition be-
 475 comes

$$-n_{sh} \cdot j_{e,sh} = n_{pp} \cdot j_{e,pp} + s_{r,out} j_{r,out}, \quad \text{on } \partial\Omega_{pp}. \quad (35)$$

476 The first term on the right-hand side of Eq. (35) represents lithium transport through
 477 open electrolyte channels connecting the particle pores to the surrounding shell,
 478 and the second term represents lithium exchange due to the outer intercalation
 479 reactions.

480 Applying the same argument to electrolyte charge balance at the particle-shell in-
 481 terface gives

$$-n_{sh} \cdot i_{e,sh} = n_{pp} \cdot i_{e,pp} + s_{r,out} F j_{r,out}, \quad \text{on } \partial\Omega_{pp}. \quad (36)$$

482 The electrolyte concentration and potential are continuous across connected elec-
 483 trolyte regions. However, microscopic simulations in Section 6.1 show that localized
 484 interfacial layers, characterized by steep concentration and potential variations, can
 485 develop near the particle-shell interface when transport pathways into internal pores
 486 are narrowed by excessive type-2 additive contacts, as schematically shown in Fig. 5.
 487 The homogenized model with surface-averaged interface conditions cannot explic-
 488 itly resolve these localized interfacial layers. Their effects are therefore represented
 489 through additional modeling closures in the form of the effective jump terms Δc_e
 490 and $\Delta\phi_e$, as

$$c_{e,pp} = c_{e,sh} + \Delta c_e, \quad \phi_{e,pp} = \phi_{e,sh} + \Delta\phi_e, \quad \text{on } \partial\Omega_{pp}. \quad (37)$$

491 These jump terms modify only the effective interface values, while mass and charge
 492 conservation remain enforced through Eqs. (35) and (36).

493 To represent the unresolved potential drop between outer reaction sites and the
 494 conductive-additive contact, we define the contact potential $\phi_{s,cc}$ by

$$\phi_{s,cc} = \phi_{s,r,out} + \Delta\phi_s, \quad \text{on } \partial\Omega_{pp}, \quad (38)$$

495 where $\phi_{s,r,out}$ denotes the AM potential on the outer intercalation surface, evaluated
 496 from the homogenized solution $\phi_{s,pp}$ on $\partial\Omega_{pp}$. The term $\Delta\phi_s$ represents the corre-
 497 sponding surface-averaged potential drop to the type-1 contacts and accounts for the
 498 localized microscale electronic transport limitations caused by the finite and spatially
 499 heterogeneous conductive additive contact area. In the general homogenized formu-
 500 lation, the introduced jump terms may be time dependent. For the constant-current
 501 benchmark considered in this study, the particular closures employed are calibrated
 502 using time-averaged differences obtained from the corresponding 3D simulations.
 503 The physical basis of the jump terms and the adopted calibration procedure here,
 504 are described in Section 6.2.

505 Finally, the surface-averaged electrolyte boundary conditions at the lithium-metal
 506 anode are imposed on the external shell boundary Γ_{Li} . Let n_{sh} denote the outward

normal of Ω_{sh} on Γ_{Li} . The molar reaction flux $j_{r,\text{Li}}$ is evaluated using the Butler–Volmer relation in Eq. (16), with electrolyte concentration and potential obtained from the homogenized model, leading to

$$-n_{\text{sh}} \cdot j_{e,\text{sh}} = j_{r,\text{Li}}, \quad -n_{\text{sh}} \cdot i_{e,\text{sh}} = Fj_{r,\text{Li}}, \quad \text{on } \Gamma_{\text{Li}}. \quad (39)$$

For the present benchmark, the surface-averaged interface conditions are combined with the approximately isotropic transport tensors discussed in Section 5.2. This yields an angularly averaged 1D radial formulation in which the field variables depend only on the radial coordinate. Zero normal derivatives are imposed at the particle center. The accuracy of this radial approximation is assessed a posteriori by comparison with the corresponding 3D microstructure-resolved simulations.

5. Numerical implementation and simulation setup

5.1. Finite element implementation

Both the microstructure-resolved and homogenized models are implemented in finite-element package COMSOL Multiphysics [63]. The 3D model uses the Lithium-Ion Battery interface together with the Transport of Diluted Species interface for lithium diffusion in the AM. Spatial discretization uses tetrahedral elements with linear Lagrange shape functions. The liquid- and solid-phase equations are solved in a segregated scheme with a multigrid iterative solver and successive over-relaxation (SOR) pre- and post-smoothing. For the homogenized 1D model, the weak formulation of Section 4.3 is implemented with the Weak Form PDE interface [38, 64]. For this purpose, the homogenized equations are implemented under two interconnected nodes representing the electrolyte shell and the porous particle, while using the weak contribution to enforce interface conditions. The resulting fully coupled system is solved with PARDISO using cubic Lagrange elements. For temporal discretization, both models use implicit variable-step backward differentiation formulas (BDF). The auxiliary cell problem (A.12) used to compute the macroscopic transport tensors is also implemented in COMSOL, using the Coefficient Form PDE interface, linear Lagrange elements, and PARDISO direct solver.

5.2. Microscopic domain and periodic cell construction

The computational domains are constructed from microstructural image stacks with a voxel size of 40 nm. Multi-domain tetrahedral meshes comprising the AM, electrolyte, and additive phases are generated in Simpleware ScanIP and exported, together with the phase boundaries and interfaces, in Nastran format for subsequent simulations in COMSOL Multiphysics.

The mesh settings used for microscopic simulations are determined through a mesh convergence study, described in Appendix B. Similar settings are used to compute macroscopic property tensors based on Eq. (A.12). For this purpose, the representative volume (RV) of each microstructure is determined as the minimum volume beyond which variations in the effective properties become negligible. To construct the periodic cell, a cubic subvolume is extracted from the interior of the particle

and mirrored with respect to three mutually orthogonal planes. This construction ensures that the resulting microstructure matches on each pair of opposite faces and can therefore be used as a periodic cell for the homogenization problem. The results of macroscopic property tensors for different particle types are shown in Fig. 8, both for AM and electrolyte phases.

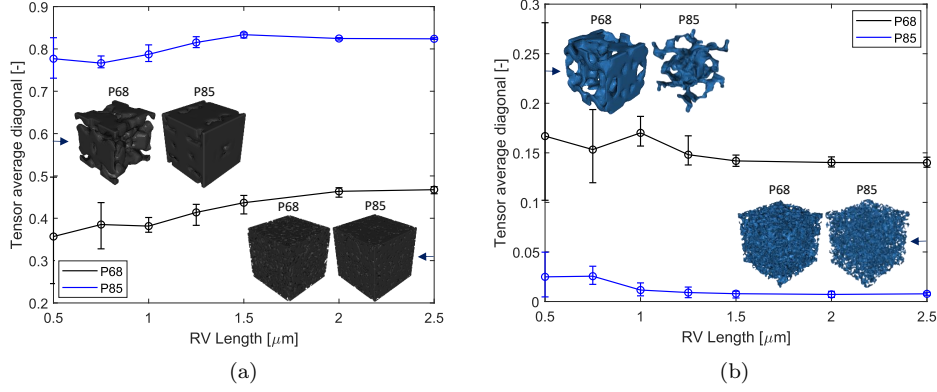


Figure 8: Representative volumes (RVs) of the microstructures used in periodic cell problems for evaluating macroscopic property tensors of active material (a) and electrolyte (b). The microstructures of the P68s and P68l particles are collectively referred to as P68, while P85 denotes the microstructures of the P85s and P85l particles described in Section 3.2.

Each point in Fig. 8 is the mean of the diagonal tensor entries. The error bars quantify the spread between the smallest and largest diagonal entries relative to that mean and therefore provide an indicator of anisotropy. For larger sampled volumes this spread decreases, supporting the approximately isotropic treatment used in the 1D model. Increasing the RV edge length beyond $2\mu\text{m}$ changes the mean effective property by less than 5%. We therefore use an edge length of $2\mu\text{m}$ for the transport-property calculations. The selected RV edge length is a numerical sampling scale for estimating the effective tensors and should not be identified with the microscopic length l in the homogenization parameter $\varepsilon = l/L$.

5.3. Material properties and simulation setup

The models presented in this paper allow direct usage of the intrinsic material properties, instead of estimating the effective properties. To investigate the ionic and electrical transport mechanisms within secondary particles and to benchmark the homogenized model over a broad transport range, various combinations of intrinsic diffusion coefficient and electrical conductivity for the cathode AM are considered, as detailed in Table 3. These properties span two orders of magnitude based on reported literature values and are used to identify transport limitation under the investigated 5C discharge conditions [42, 65, 66]. For this purpose we consider $D_s \in \{10^{-15}, 10^{-14}\} \text{ m}^2/\text{s}$ and $\sigma_s \in \{10^{-4}, 10^{-3}\} \text{ S/m}$. Although both properties depend on temperature and lithiation state, they are treated here as constant material parameters in order to separate their effects from those arising from the AM microstructure and additive distribution, thereby enabling a systematic analysis of their influence on electrochemical transport behavior. To facilitate identification of

the material properties, we denote a parameter pair by $Dx\sigma y$, where x and y are the absolute base-10 exponents. For example, $D15\sigma 4$ denotes $D_s = 10^{-15} \text{ m}^2/\text{s}$ and $\sigma_s = 10^{-4} \text{ S/m}$.

Parameter	Number	Description
Particle types	6	According to Section 3.2
Additive distribution	6-8	According to Section 3.3
Realizations	3-4	Including a full domain for small particles
AM ionic diffusion	2	$10^{-15} \text{ m}^2/\text{s}$ and $10^{-14} \text{ m}^2/\text{s}$
AM electrical conductivity	2	10^{-4} S/m and 10^{-3} S/m

Table 3: Parameters of the performed 3D microscopic simulations. For non-porous particles, the additive configurations S50 and S95 are equivalent to A50 and A95, respectively. Furthermore, full-domain simulations for large particles are excluded due to their extensive computational demands.

To sample variability in the virtually generated particle microstructure and surface additives, multiple realizations are simulated. Taking advantage of the general symmetry of the particle microstructure, three distinct chunks of cathode particles, as illustrated in Fig. B.20a, are considered using symmetric boundary conditions on the cutting planes. Additionally, one full-particle simulation is performed for small cathode particles. The mesh study in Appendix B shows that a P68s one-eighth domain already contains approximately 1.9 million elements, whereas a full small-particle domain contains about 15 million. For the larger particles, the corresponding full-domain size increases by approximately a factor of eight and is therefore not used in the parameter sweep. A representative simulation for the P68s particle with A35 surface configuration and $D15\sigma 4$ material properties requires approximately 1.3 h for a one-eighth domain and 17.2 h for the full small-particle domain on a Lenovo ThinkSystem SR650 cluster with four 64-CPU, 256-GB nodes. The complete study comprises 576 microscopic simulations. For each case, a corresponding 1D homogenized simulation with the same geometric descriptors and intrinsic material parameters is performed, completing in about a minute on a standard laptop².

6. Results and model benchmarking

All simulations in this section use a 5C discharge rate and a 3.3 V cut-off voltage, evaluated on the electrical contacts. The applied current for each particle realization is calculated based on the prescribed C-rate and the particle reference capacity, determined from the AM volume and the lithium concentration limits $c_{s,\min}$ and $c_{s,\max}$, given in Table 2. We first illustrate the local transport mechanisms for a representative low-diffusivity, low-conductivity case, based on the 3D microscopic simulation results. We then compare the 3D and 1D models across all AM-property combinations, particle sizes, microstructures and additive configurations listed in

²Due to differing hardware, these wall-times are illustrative, and should not be interpreted as hardware-normalized speedup factors.

Table 3. Section 6.1 evaluates the 1D homogenized model before introducing the additive-induced jump closures of Eqs. (37) and (38), Section 6.2 calibrates these closures from the 3D microscopic benchmark data, and Section 6.3 compares the resulting 1D model with the corresponding 3D cases.

6.1. 3D and 1D model results without additive-induced jump terms

Figure 9 shows the solid potential, state of lithiation (SoL), denoted as x_s , and local intercalation-current distribution on the outer and internal reaction surfaces of a P68s particle with the A5 additive configuration and $D15\sigma4$ material properties at the end of a 5C discharge. The electrical contacts appear as low-potential regions in Fig. 9a. Since intercalation reaction requires electrons supplied through the AM/additive contacts, the low AM conductivity makes electronic transport a limiting factor, leading to stronger lithiation near those contacts as shown in Fig. 9b. At the same time, low solid-state diffusivity hinders transport toward the particle core. The combination of these transport limitations creates a pronounced spatial imbalance, causing the outer regions near the electrical contacts to approach saturation while the core remains less lithiated. Consequently, the contact voltage reaches the cut-off value before the particle can be uniformly utilized. At the end of discharge, as illustrated in Fig. 9c, the intercalation current on the highly lithiated outer regions is small, whereas the current on the internal surfaces remains comparatively well distributed. The radial variations of SoL and solid potential affect the local overpotential in opposing directions and therefore partially compensate in the reaction kinetics.

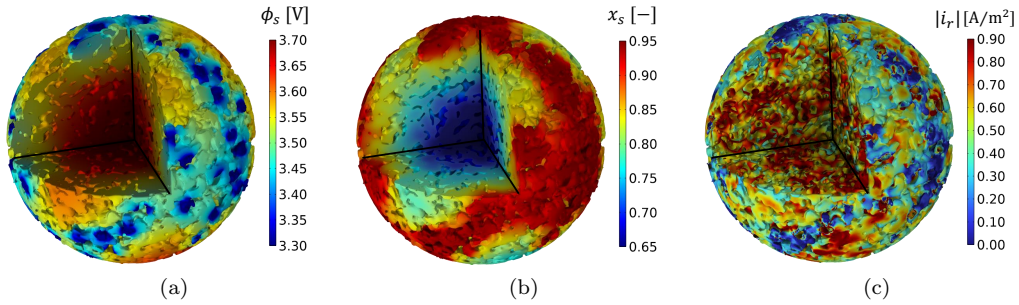


Figure 9: Microstructure-resolved results at the end of discharge for a full P68s particle with the A5 additive configuration and $D15\sigma4$ material properties: (a) solid potential, (b) local state of lithiation, and (c) magnitude of the intercalation current density on the reaction surfaces Γ_{se} .

Figure 10 presents the surface-averaged potential values across all investigated additive configurations and particle realizations, evaluated against the volume-averaged SoL ($\bar{x}_s$) within a P68s particle. As depicted in Fig. 10a, the cell potential, defined here as the solid-phase potential averaged over the electrical contact surface Γ_{cc} , strongly depends on the additive configuration. In contrast, the solid-phase potential averaged over the outer intercalation surface $\Gamma_{r,out}$, shown in Fig. 10b, exhibits only a weak dependence on the additive configuration. In the 3D simulation, the surface potential drop is defined by

$$\Delta\phi_s^{3D}(t) = \phi_{s,cc}^{3D}(t) - \phi_{s,r,out}^{3D}(t), \quad (40)$$

where $\phi_{s,cc}^{3D}(t)$ and $\phi_{s,r,out}^{3D}(t)$ denote the solid-phase potentials averaged over Γ_{cc} and $\Gamma_{r,out}$, respectively. Figure 10c shows that $|\Delta\phi_s^{3D}|$ magnitude generally increases as additive coverage decreases. The scatter among realizations reflects the random spatial arrangement of the additives and the resulting differences in surface coverage. The relationship between the potential drop and the additive distribution is examined in more detail in Section 6.2.

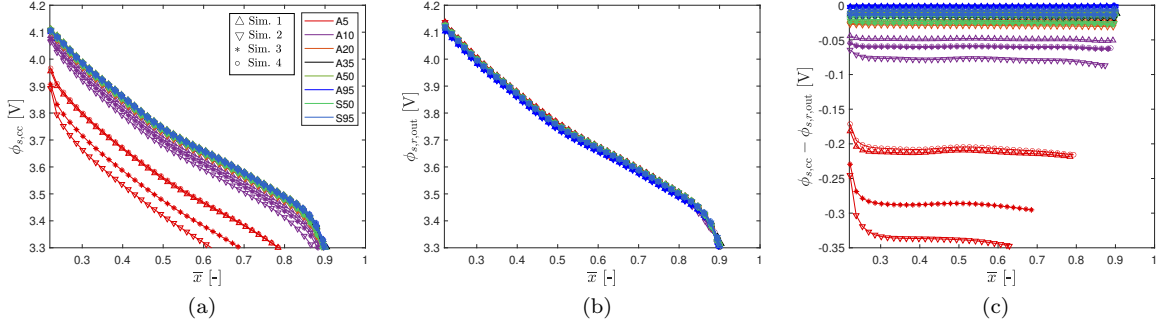


Figure 10: Microscopic simulation results of solid-phase potential for all simulated realizations and additive configurations of a P68s particle with $D15\sigma4$ material properties. Subfigures show surface-averaged potentials on (a) Γ_{cc} , (b) $\Gamma_{r,out}$, and (c) their difference.

In the following, the 3D microscopic benchmark and the corresponding 1D homogenized simulation results are compared. In this section, the additive-dependent geometric surface fractions of Section 4.3 are retained, but the jump closures in Eqs. (37) and (38) are set to zero. Those closure terms are quantified in Section 6.2, and incorporated in the performed simulations of Section 6.3.

Figure 11 shows close agreement between the 3D and 1D predictions of $\phi_{s,r,out}$ over the investigated additive coverages. Nevertheless, low additive coverage leads to a smaller attainable volume-averaged SoL because sparse electronic contacts increase the potential drop between Γ_{cc} and the outer reaction surface, causing the contact voltage to reach the cut-off earlier. Therefore, accurate prediction of the achievable discharge capacity in the homogenized model requires accounting for the surface potential drop in the calculation of $\phi_{s,cc}$, particularly at low s_{cc} .

Figure 12 compares radial concentration and potential profiles in the AM and electrolyte phases for one P68s realization with A5, A35, and A95 additive configurations at the end of the 5C discharge. The error bars in the 3D microscopic results, represent the standard deviation of the sampled values at a given radius, while the circles indicate the corresponding mean values³. The observed radial scatter reflects unresolved microstructural heterogeneity and, particularly near the particle surface, by local variations in the distribution of conductive additives. For A5, sparse and spatially separated electronic contacts produce substantial local variation in x_s and

³Sampling lines originate at the particle center and extend along directions $\mathbf{d} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$, with $\mathbf{i}, \mathbf{j}, \mathbf{k}$ as Cartesian basis vectors where $(x, y, z) \in \{-1, 0, 1\}^3 \setminus (0, 0, 0)$, resulting in 26 sampling lines for a full particle. Analogously, 7 sampling lines are used for a one-eighth particle chunk.

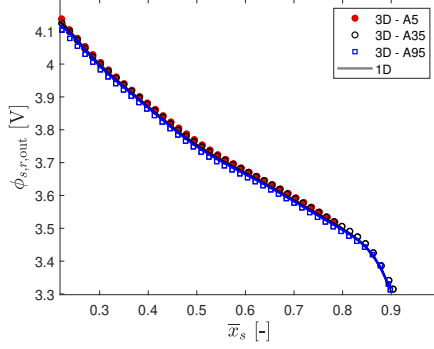


Figure 11: Comparison of $\phi_{s,r,out}$ obtained from the microscopic and 1D homogenized simulations for the Sim. 1 realization of the P68s particle, shown in Fig. 10b, with $D15\sigma4$ material properties.

658 ϕ_s , yet the 1D solution tracks the 3D radial means. At the opposite extreme, A95
 659 strongly restricts access to pore openings and produces localized electrolyte interfa-
 660 cial layers with steep variations in c_e and ϕ_e near the particle boundary. The net
 661 effects of these unresolved layers motivate the closures quantified in Section 6.2. The
 662 intermediate A35 case exhibits comparatively small localized surface effects and is
 663 therefore used for the broader particle/property comparison in Fig. 13.

664 Figure 13 examines the combined influence of AM transport properties and particle
 665 microstructure. For this comparison, an auxiliary porous particle with 90% AM
 666 volume fraction (P90s) is added to the previously defined particle set. The P90s
 667 particle is generated with the stochastic microstructure model using $\gamma = 0.9$ and
 668 $r = 4.4\mu\text{m}$, as described in Section 3.1.2. Despite the simplifying assumptions
 669 underlying the homogenization theory, the 1D predictions reproduce the principal
 670 3D trends in SoL distribution, local cell potential, and discharge capacity for the
 671 cases shown. For bulk particles, low AM diffusivity is the dominant limitation
 672 because lithium must penetrate from the outer surface. In the low-diffusivity P100s
 673 case, less than 40% of the AM is lithiated when the cut-off voltage is reached,
 674 whereas the porous particles exceed 80% owing to additional electrolyte pathways
 675 and internal reaction surfaces. Electronic conductivity has a stronger influence
 676 in porous particles as electrons must be transported through the AM network to
 677 sustain the intercalation reaction on internal surfaces. As shown in the left-column of
 678 Fig. 13, the highly porous P68s particle exhibits an almost uniform SoL distribution
 679 under high-conductivity conditions, resulting in nearly complete lithiation of the
 680 particle. Increased porosity, however, reduces AM loading. At 5C, it can be observed
 681 that the P85s provides the highest discharge capacity among the porous particles
 682 even though P68s can achieve higher particle utilization.

683 6.2. Calibration of additive-induced jump terms for homogenized 1D models

684 As described in Section 4.3, the homogenized 1D model cannot resolve the local-
 685 ized interfacial layers caused by distributed additive contacts at the secondary-
 686 particle surface. We therefore represent their net effects through the jump closures
 687 in Eqs. (37) and (38). In this section, the closure terms are calibrated for the

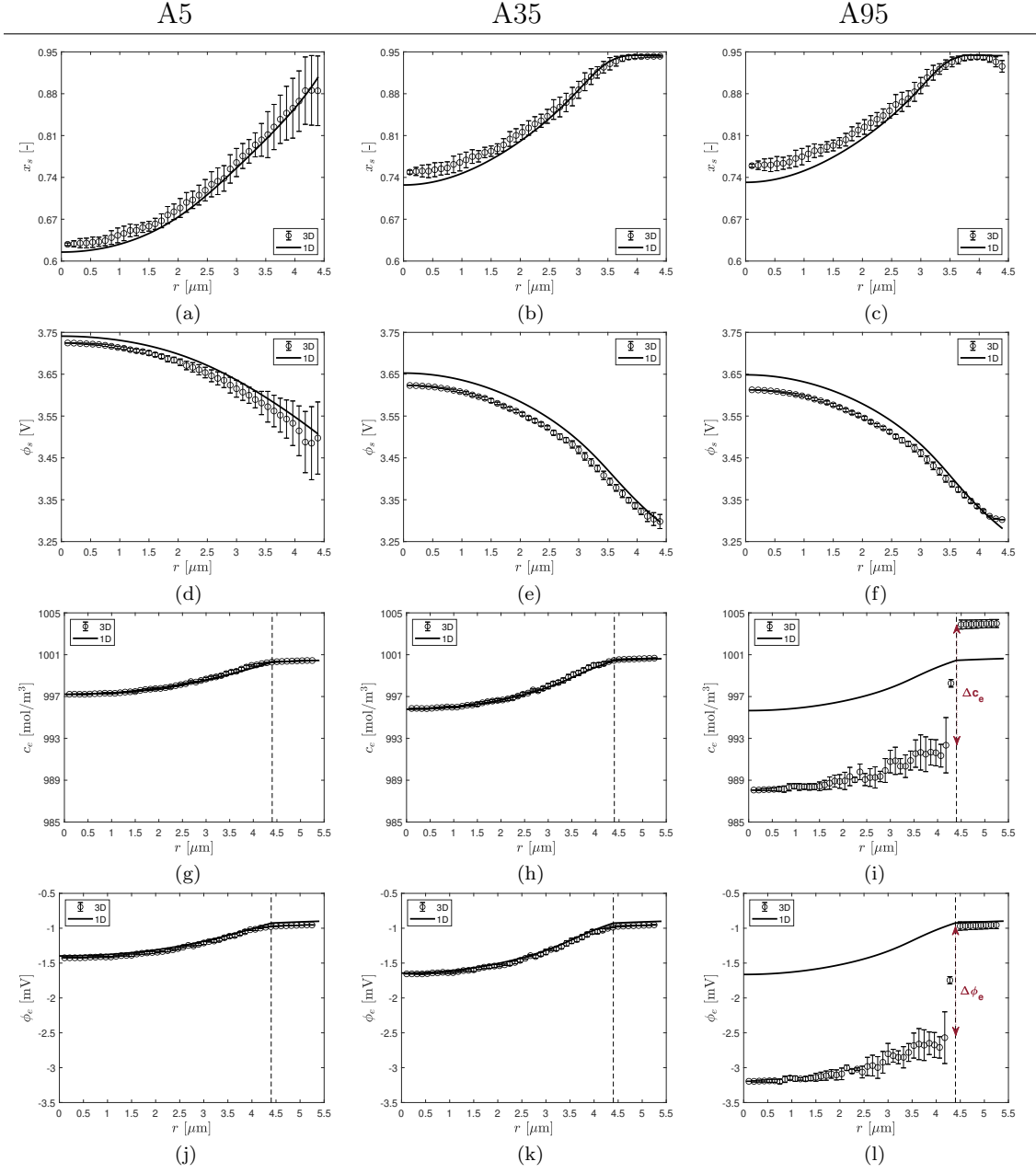


Figure 12: Comparison of microscopic and 1D homogenized simulation results for a P68s particle with A5, A35, and A95 surface configurations with $D15\sigma4$ material properties, excluding additive jump terms. Subfigures show radial distributions of (a–c) SoL; (d–f) solid potential; (g–i) electrolyte concentration; and (j–l) electrolyte potential at the end of discharge. Here, $r = 0$ denotes the particle center, and the dashed line at $r = 4.4 \mu\text{m}$ in the electrolyte fields indicates the mean outer particle radius.

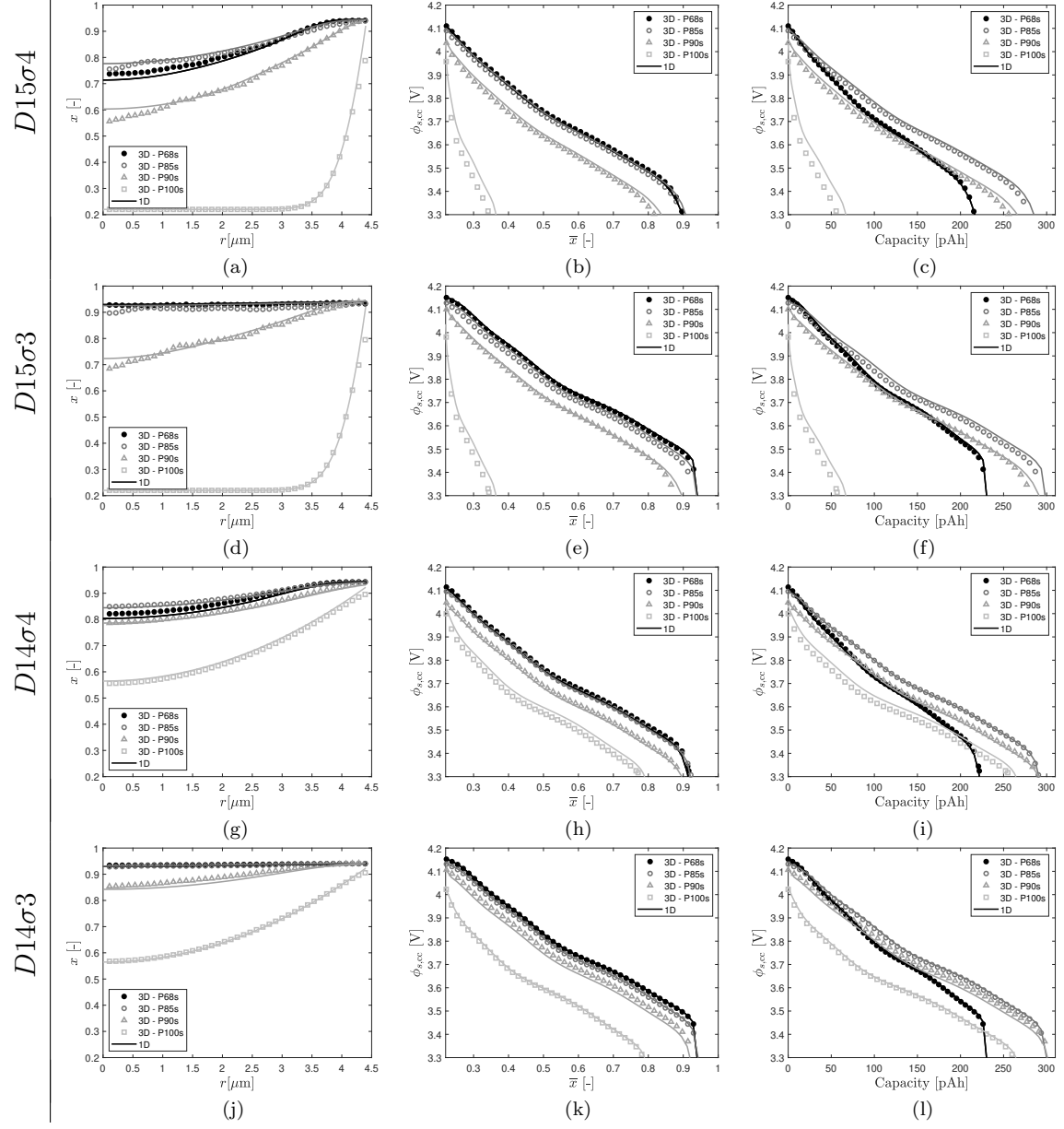


Figure 13: Comparison of microstructure-resolved and 1D homogenized simulations for different particles and AM properties with the A35 additive configuration. The left, middle, and right columns present radial SoL profiles, contact potential versus volume-averaged SoL, and contact potential versus discharge capacity, respectively.

constant-current benchmark considered in this study, based on the corresponding 3D simulation results. To differentiate between quantities obtained directly from the 3D simulations and the jump terms employed in the 1D model, the former are denoted by $\Delta\phi_s^{3D}(t)$, $\Delta c_e^{3D}(t)$, and $\Delta\phi_e^{3D}(t)$.

Intercalation requires electronic current to reach AM/electrolyte reaction sites from the conductive-additive contacts. As illustrated in Fig. 14a, current feeding outer reaction sites travels mainly along the near-surface AM, whereas the remaining current is directed toward internal reaction surfaces. Sparse additive coverage increases the typical distance between electrical contacts and outer reaction sites and therefore increases the effective surface resistance. This geometric dependence is consistent with classical and micro-contact resistance studies, which show increasing resistance with contact spacing and decreasing resistance with increasing contact area [67, 68, 69, 70, 71, 72].

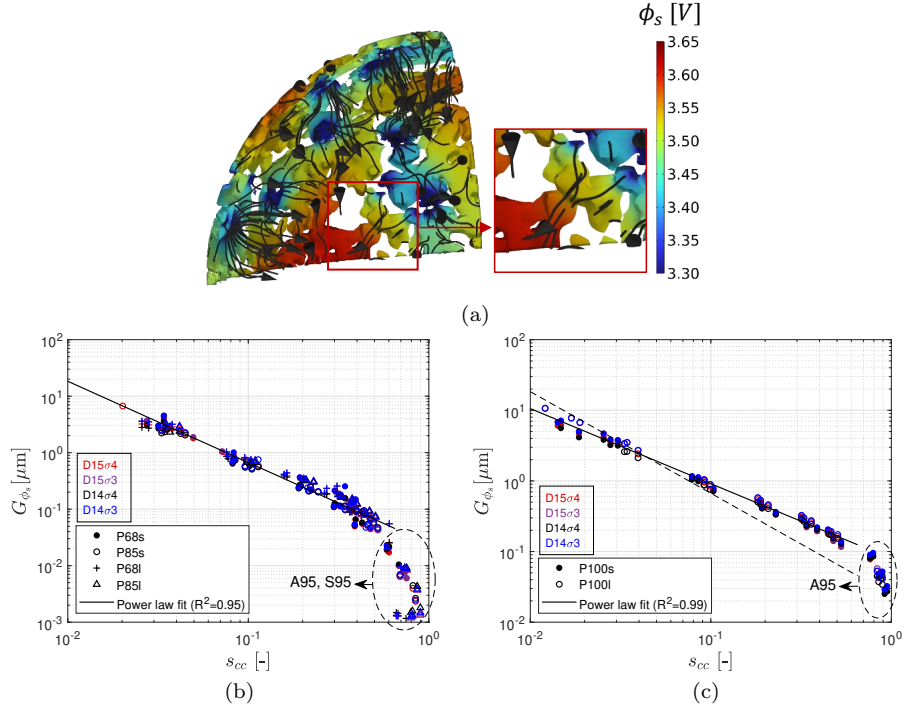


Figure 14: (a) Solid-phase potential distribution in a P68s particle with the A5 surface configuration and $D15\sigma4$ material properties at the end of discharge, with black arrows indicating electron transport pathways. Surface resistance length scale as a function of s_{cc} for microscopic simulations of (b) porous and (c) bulk particles. Each point represents one simulation, and the dashed line in (c) shows the G_{ϕ_s} function fitted to the porous-particle results for comparison.

Motivated by this behavior, we define the surface resistance length scale G_{ϕ_s} based on the time-averaged 3D surface-potential difference $\Delta\phi_s^{3D}$ over the discharge, denoted by $\overline{\Delta\phi_s^{3D}}$, as

$$G_{\phi_s} = -\frac{\sigma_s \overline{\Delta\phi_s^{3D}}}{i_{app}}. \quad (41)$$

Figures 14b and 14c present the corresponding results for 432 porous and 144 bulk

particle simulations. The results indicate that within the investigated parameter range, G_{ϕ_s} is only weakly dependent on AM diffusivity, electrical conductivity, volume fraction, particle radius, and the surface ratio of electrolyte open channels, whereas the distribution of adhered conductive additives on the AM is identified as the dominant influencing factor.

For the A95 and S95 configurations ($s_{cc} > 0.65$), the surface potential difference falls below 15 mV for porous particles and 62 mV for bulk particles even at 5C with $\sigma_s = 10^{-4}$ S/m. Increasing the conductivity σ_s to 10^{-3} S/m reduces these differences by approximately one order of magnitude. In the present closure, this high-coverage regime is therefore approximated by $G_{\phi_s} = 0$. For $s_{cc} \leq 0.65$, power-law fits give $R^2 = 0.95$ for porous particles and $R^2 = 0.99$ for bulk particles. Therefore, for porous particles with $s_{cc} \leq 0.65$, we obtain

$$G_{\phi_s} = 0.0244 \mu\text{m} s_{cc}^{-1.4383}, \quad (42)$$

and, for bulk particles, G_{ϕ_s} quantifies as

$$G_{\phi_s} = 0.0789 \mu\text{m} s_{cc}^{-1.0634}. \quad (43)$$

At low s_{cc} , porous particles exhibit larger G_{ϕ_s} than bulk particles because the tortuous AM network lengthens electronic paths from sparse contacts to neighboring outer reaction sites. At high s_{cc} , this trend reverses. With increasing conductive additive content, the contribution of the outer surfaces to total lithium intercalation decreases as a larger fraction of the reaction current is carried by internal surfaces, as further discussed in Section 6.3. This reduces the local electronic current density at the outer surface and thereby mitigates the associated surface potential drop, despite the tortuous transport pathways within the AM network.

The distribution of additives also affects electrolyte transport. Partial blockage of pore openings concentrates the electrolyte flux into the remaining open channels, producing stronger local concentration and potential gradients near the particle boundary. This behavior is illustrated in Figs. 12i and 12l. Analogous to the solid-phase surface potential drop, we define the surface gradient length scales G_{c_e} and G_{ϕ_e} based on the time-averaged 3D electrolyte differences as

$$G_{c_e} = -\frac{FD_e \overline{\Delta c_e^{3D}}}{i_{\text{app}}}, \quad G_{\phi_e} = -\frac{\sigma_e \overline{\Delta \phi_e^{3D}}}{i_{\text{app}}}, \quad (44)$$

where the 3D quantities are defined by

$$\Delta c_e^{3D}(t) = c_{e,\text{pp}}^{3D}(t) - c_{e,\text{sh}}^{3D}(t), \quad \Delta \phi_e^{3D}(t) = \phi_{e,\text{pp}}^{3D}(t) - \phi_{e,\text{sh}}^{3D}(t),$$

and represent the differences between the corresponding surface-averaged electrolyte concentrations and potentials across the predefined shell in Fig. 4a. The barred quantities denote their respective time averages over the discharge.

736 The corresponding length scales, shown in Figs. 15a and 15b, demonstrate that the
 737 open-channel fraction s_{open} is a prominent influencing factor of G_{c_e} and G_{ϕ_e} . Over
 738 the observed range $s_{\text{open}} \leq 0.32$, power-law fits give moderate-to-strong correlations
 739 of G_{c_e} and G_{ϕ_e} with s_{open} , with R^2 values of 0.80 and 0.78, respectively⁴. This
 740 indicate that reduced pore accessibility hinders electrolyte transport into the particle
 741 interior, leading to lower lithium-ion concentrations and electrolyte potentials. The
 742 resulting closures are

$$G_{c_e} = 0.1270 \mu\text{m} s_{\text{open}}^{-1.2246}, \quad G_{\phi_e} = 1.3329 \mu\text{m} s_{\text{open}}^{-1.1749}. \quad (45)$$

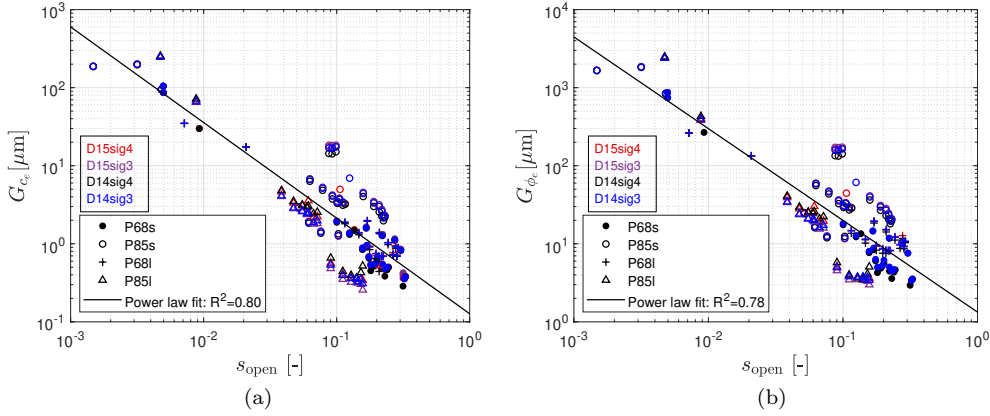


Figure 15: Surface gradient length scales for (a) electrolyte concentration, and (b) potential drops, as functions of s_{open} for all microscopic porous particle simulations, where each point represents one simulation.

743 The results consistently demonstrate that, within the sampled parameter range, the
 744 additive-induced jump length scales depend more strongly on the surface geometry
 745 than on particle size or the intrinsic AM properties. Incorporating G_{ϕ_s} enables
 746 the 1D model to reconstruct the contact potential, while G_{c_e} and G_{ϕ_e} correct the
 747 electrolyte fields that control internal reaction kinetics. For the constant-current
 748 benchmark considered here, the fitted length scales are converted into the effective
 749 jump values used in the 1D model according to

$$\Delta\phi_s = -\frac{i_{\text{app}}}{\sigma_s} G_{\phi_s}, \quad \Delta c_e = -\frac{i_{\text{app}}}{F D_e} G_{c_e}, \quad \Delta\phi_e = -\frac{i_{\text{app}}}{\sigma_e} G_{\phi_e}.$$

750 For evaluation of the length scales, if image-resolved surface fractions are unavail-
 751 able, a first-order approximation is $s_{cc} \approx s_{\text{add}} \varepsilon_{s,\text{pp}}$, $s_{r,\text{out}} \approx (1 - s_{\text{add}}) \varepsilon_{s,\text{pp}}$, and
 752 $s_{\text{open}} \approx (1 - s_{\text{add}}) \varepsilon_{e,\text{pp}}$, where s_{add} is the fraction of outer particle surface cov-
 753 ered by conductive additives.⁵ The simulations reported here, however, use the

⁴The maximum s_{open} value of 0.32 corresponds to the local interfacial surface porosity of the P68s and P68l particles, whereas the smallest s_{open} values occur for P85s and P85l. The full set of surface ratios is shown in Fig. 6.

⁵For bulk particles, the solid-phase volume fraction equals 1.

image-derived fractions in Fig. 6. Although the jump terms in the general interface conditions may be time dependent, the present calibration provides effective jump values for the constant-current simulations considered in this work. Extending the calibration to genuinely time-dependent operating conditions is beyond the scope of the present benchmark.

6.3. 3D and 1D model comparison with calibrated additive-induced jump terms

In the following, we compare the homogenized 1D model incorporating the calibrated additive closure terms of Section 6.2, with the corresponding 3D reference simulations and examine the coupled transport mechanisms in porous and bulk particles.

As observed in Figs. 14 and 15, the strongest additive-induced effects on surface resistance and electrolyte gradients occur for small s_{cc} and s_{open} surface ratios, respectively, which correspond to particles with A5 and A95 additive configurations. Figure 16 compares the performance of the 1D model incorporating the proposed jump terms with the reference 3D simulations for these additive configurations in a porous particle representation.

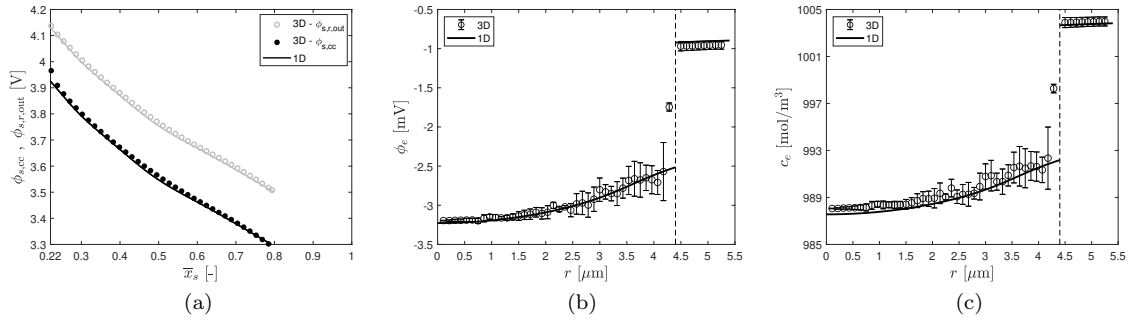


Figure 16: Comparison of microscopic and 1D homogenized simulation results for $D15\sigma4$ material properties. (a) The contact and outer-reaction-surface solid potentials versus SoL for A5; (b) electrolyte potential and (c) electrolyte concentration at the end of discharge for A95. Error bars in the microscopic results denote the standard deviation of sampled values at a given radius.

Accurate reconstruction of the potential at the AM/additive contact is particularly relevant to future electrode-scale modeling, as this quantity provides the coupling between particle-scale electronic transport and the surrounding conductive network. Figure 16a shows that, for the A5 configuration with highly dispersed electrical contacts, the interfacial potentials obtained from the homogenized 1D model are in good agreement with the 3D results, with a maximum deviation of 41 mV at the beginning of discharge. As shown in Figs. 16b and 16c, the model also reproduces the electrolyte potential and concentration jumps arising from the strongly obstructed surface of the A95 configuration.

Increasing additive coverage reduces the accessible outer intercalation area $\Gamma_{r,out}$ and shifts a larger fraction of the reaction toward the internal interface $\Gamma_{r,in}$. Sustaining the increased reaction current at the internal interface, correspondingly requires higher electrolyte mass and charge transport through the open pore mouths. The

interplay between the reaction and transport pathways is described by the interface conditions in Eqs. (35) and (36). To quantify the relative contributions of the two intercalation interfaces with respect to the applied current I_{app} , we evaluate the outer-surface reaction current in the microscopic model as

$$I_{r,\text{out}} = F \int_{\Gamma_{r,\text{out}}} \hat{j}_r(x, t) ds.$$

The corresponding outer-surface contribution in the homogenized model is $I_{r,\text{out}} = F|\Gamma_{r,\text{out}}|j_{r,\text{out}}$.

As illustrated in Fig. 17, increasing additive coverage decreases the contribution of the outer-surface reaction current, as reflected by the reduction in $I_{r,\text{out}}/I_{\text{app}}$, while increasing the magnitude of the outer-surface overpotential. For all additive configurations, the fractional contribution from the outer surface is highest early in the discharge and then remains comparatively stable over the intermediate SoL range. At high SoL, outer-surface saturation and the associated increase in overpotential shift the reaction toward internal surfaces. The 1D model reproduces these trends as well as the corresponding outer-surface overpotentials despite not resolving the local heterogeneity explicitly.

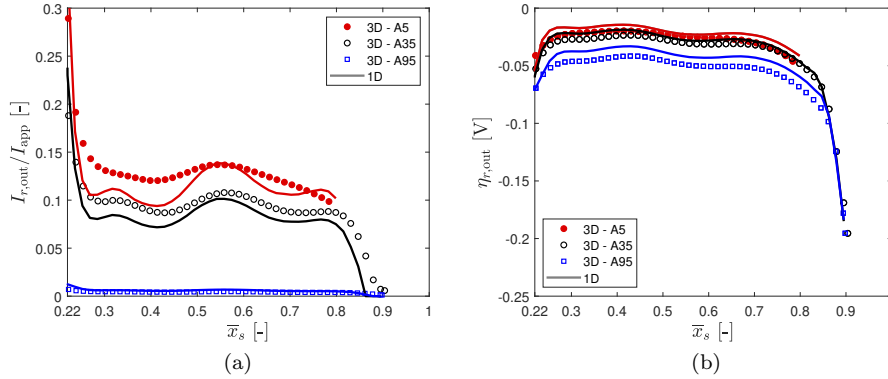


Figure 17: Comparison of microscopic and 1D homogenized results for different porous particles and additive configurations with $D15\sigma4$ material properties. (a) The ratio of outer-surface to total reaction current, and (b) the corresponding outer-surface overpotential, both as functions of SoL.

The outer-surface current fraction depends not only on SoL but also on the intrinsic AM properties. Figure 18 summarizes the time-averaged ratio $\bar{I}_{r,\text{out}}/I_{\text{app}}$ for all considered porous particles and material-property combinations during 5C discharge. Across the investigated cases, $\bar{I}_{r,\text{out}}/I_{\text{app}}$ varies approximately linearly with the respective geometric area fraction $|\Gamma_{r,\text{out}}|/|\Gamma_{se}|$, a trend which is also captured by the 1D homogenized model. The dashed reference line corresponds to reaction current distributed in direct proportion to available reaction area, and the points below that line indicate a comparatively stronger contribution from internal surfaces.

Figure 18 shows that the enhancement of AM lithiation by porous particles relative to bulk particles is most pronounced when solid-state diffusivity is low and

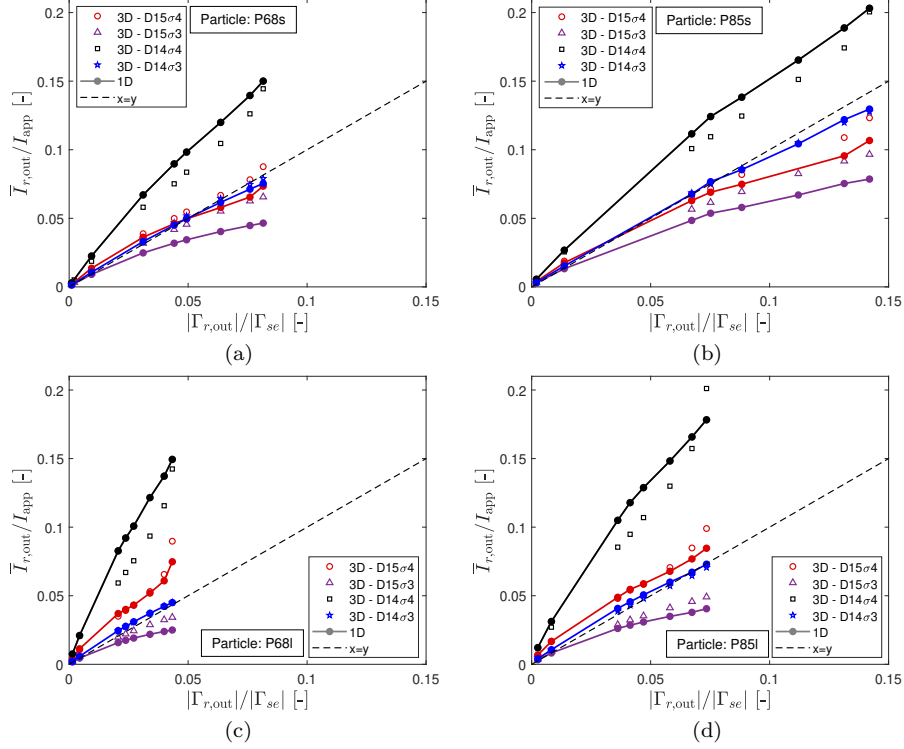


Figure 18: Comparison of microstructure-resolved and 1D homogenized results for all porous-particle types, AM-property combinations, and additive configurations. Each point shows the time-averaged outer-reaction current fraction $\bar{I}_{r,out}/I_{app}$ versus the corresponding outer-reaction area fraction for the particle types (a) P68s, (b) P85s, (c) P68l, and (d) P85l.

electronic conductivity is sufficiently high. Low D_s leads to lithium accumulation near the outer surface and limits further lithiation over long solid-state diffusion distances. The electrolyte-filled pore network bypasses these distances and thereby promotes lithium uptake at the internal surfaces. In contrast, low σ_s restricts electron transport through the AM network and suppresses intercalation at the internal surfaces, a limitation which becomes more pronounced for larger particles. When both D_s and σ_s are high ($D14\sigma3$), the reaction current is distributed approximately in proportion to the available reaction area, and the points therefore lie close to the dashed reference line. For the $D15\sigma4$ case, the benefit of internal electrolyte access in mitigating low diffusivity is increasingly offset by electronic transport limitations as the particle size increases. Accordingly, the largest and smallest internal-surface current contributions are observed for the $D15\sigma3$ and $D14\sigma4$ cases, respectively. These trends are consistent with the findings presented in Section 6.1 and with previous agglomerate-model observations [41].

Conductive additives influence the particle response through competing mechanisms. They establish electronic contact, but they also cover outer reaction sites and can obstruct electrolyte access to the internal pores. At the electrode level, the additive phase can additionally increase the tortuosity of the electrolyte transport pathways within the electrolyte/additive matrix [21, 28]. Figure 19 summarizes the com-

827 bined effects of AM particle design, additive configuration, and intrinsic material
 828 properties on particle utilization, quantified here by the volume-averaged SoL at
 829 the end of discharge. Increasing s_{cc} initially improves AM utilization by reducing
 830 the surface resistance between the electrical contacts and the outer intercalation
 831 surfaces, as discussed in Section 6.2. At higher additive contents, however, this
 832 benefit either saturates or is outweighed by the loss of accessible reaction area and
 833 restricted electrolyte access, leading to lower final utilization. The non-monotonic
 834 dependence on additive coverage is consistent with the observation of Oh et al.
 835 that the benefit of additional conductive carbon can saturate at high-rate operation
 836 discharge [62].

837 The benefit of porous particles arises from the additional electrolyte transport path-
 838 ways and reaction area provided by the internal pore network. However, effective
 839 utilization of the internal surfaces requires sufficient electron transport through the
 840 AM network. Accordingly, Fig. 19 shows attainable SoL values above 92% for the
 841 high-conductivity $D14\sigma3$ and $D15\sigma3$ porous-particle cases. When the electronic
 842 conductivity is low, increasing D_s provides only a moderate improvement in SoL.
 843 Although faster solid-state diffusion reduces lithium accumulation and the associ-
 844 ated overpotential magnitude near the outer surface, electron supply to the internal
 845 reaction sites remains limiting. Porous-particle utilization is therefore governed pre-
 846 dominantly by electronic transport. In contrast, the utilization of bulk particles
 847 is limited primarily by solid-state diffusion, particularly at larger particle radii, as
 848 shown in Fig. 13. In bulk particles, the impact of low electronic conductivity arises
 849 predominantly from increased surface resistance and can therefore be partially mit-
 850 igated by increasing the conductive-additive coverage, thereby delaying premature
 851 voltage cut-off.

852 The largest utilization gain occurs for large particles with low diffusivity and high
 853 electronic conductivity. In this case, the retained SoL increases from a maximum
 854 of 26% for P100l to more than 92% for the porous P68l and P85l particles. No-
 855 tably, the SoL values obtained for porous particles with the S50 and S95 additive
 856 configurations are comparable to those obtained with the corresponding A50 and
 857 A95 configurations. This similarity indicates that, within the investigated param-
 858 eter range, the electrical-contact surface ratio is the dominant geometric descriptor
 859 of the additive phase. A slight reduction in SoL from S95 to A95 is observed for
 860 the P85s and P85l particles, which can be attributed to the additional restriction
 861 of electrolyte transport imposed by the type-2 additive contacts. Given that the
 862 diffusion coefficient in the electrolyte phase is orders of magnitude higher than that
 863 in the AM phase, the modest magnitude of this reduction implies that the remaining
 864 open-mouth surfaces in the A95 configuration are sufficient to sustain the required
 865 transport processes within the electrolyte phase.

866 Overall, the homogenized 1D model reproduces the principal 3D trends across par-
 867 ticle microstructures, additive coverage, and AM transport properties, while sub-
 868 stantially reducing the computational burden. Within the investigated benchmark,
 869 it therefore provides a computationally efficient tool for studying how particle mor-

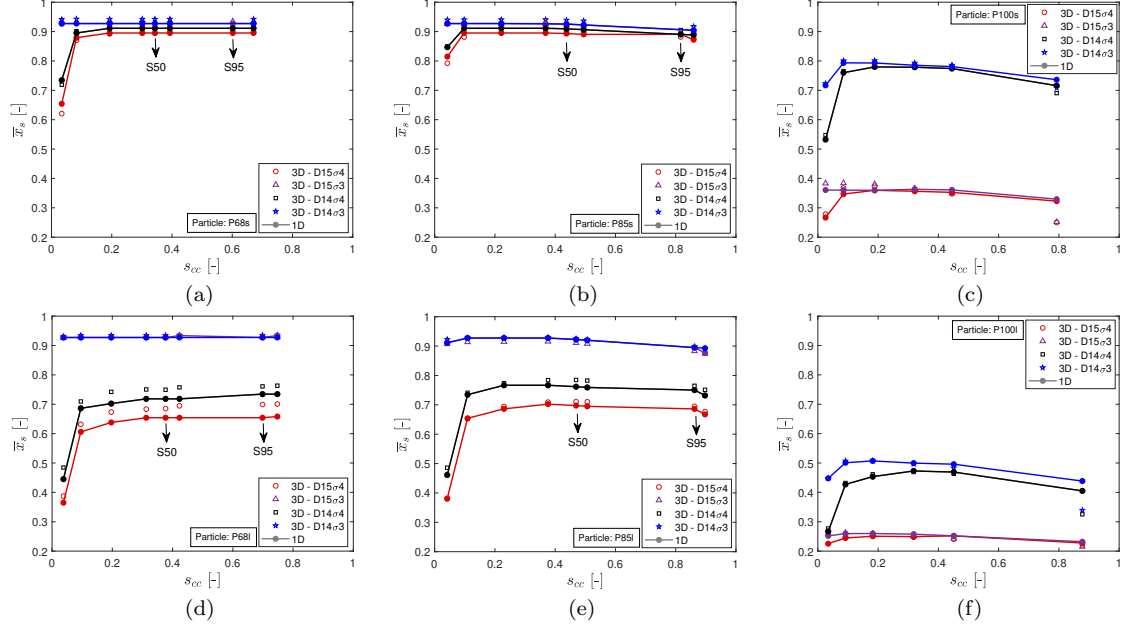


Figure 19: Comparison of microscopic and 1D homogenized simulation results for all studied particles, material properties, and additive configurations. Each point represents the volume-averaged SoL at the end of discharge plotted against s_{cc} for a (a) P68s, (b) P85s, (c) P100s, (d) P68l, (e) P85l, and (f) P100l particle.

phology and surface additive coverage influence particle-scale transport and utilization.

7. Conclusion and outlook

This study developed a 3D microstructure-resolved reference model and a computationally efficient homogenized model for porous lithium-ion cathode particles with conductive-additive surface effects. Starting from the microscopic electrochemical equations, particle-scale transport equations were derived by asymptotic homogenization. The resulting formulation combines intrinsic material properties with microstructure-dependent transport tensors obtained from representative cell problems, while surface descriptors and data-calibrated jump relations represent unresolved electronic-contact and electrolyte-access effects at the particle boundary. Across the investigated parameter space, the 1D implementation reproduces the corresponding 3D simulation results with consistently high accuracy. Once the effective transport tensors and surface closures are available, an individual 1D calculation requires about a minute compared with the hour-scale computations of the 3D reference model.

The numerical benchmark combines realistic virtual NMC porous secondary particles with controlled conductive-additive surface configurations. The particle microstructures were generated using a stochastic model calibrated to FIB-SEM tomography and extended in the present work to account for a radial variation in AM volume fraction. Virtual conductive-additive distributions were imposed on the

particle surface to systematically vary electronic contact and pore-mouth obstruction. Variations in particle size, internal microstructure, additive coverage, AM diffusivity, and electronic conductivity allow the competing effects of solid-state diffusion, electronic transport, internal porosity, electronic contact, and pore-mouth obstruction to be distinguished and their influence on active-material utilization to be quantified.

The results demonstrate the benefit of internal porosity when solid-state diffusion is slow and electronic conductivity is sufficiently high. The internal pore network shortens solid-state diffusion distances and provides additional reaction surfaces, thereby increasing AM utilization. When electronic conductivity is low, however, transport through the AM network limits electronic access to these internal reaction surfaces, particularly in larger particles, whereas the pore-closed reference particles remain predominantly limited by solid-state diffusion under low-diffusivity conditions. Conductive-additive coverage introduces an additional trade-off. Increasing the electronic contact fraction initially reduces the AM-side surface potential drop, but at higher coverage this benefit saturates, while the accessible outer reaction area decreases and pore-mouth obstruction can increase electrolyte concentration and potential gradients. Within the investigated single-particle benchmark, intermediate additive coverages therefore provide a favorable balance between electronic contact, reaction accessibility, and electrolyte transport.

The homogenized particle model provides a computationally efficient building block for simulations of hierarchically structured cathodes. At the electrode scale, it can be coupled to transport in the surrounding electrolyte and conductive-additive matrix through the particle-surface exchange quantities developed here, thereby enabling particle packing, additive-network connectivity, inactive-phase loading, and electrode-scale electrolyte tortuosity to be incorporated. This extension would allow the particle-scale trade-offs identified in the present study to be investigated in the context of electrode design and performance. Experimental assessment of the calibrated surface closures and transfer to other particle morphologies and operating conditions provide further directions for future work.

CRedit authorship contribution statement

Javid Piruzjam: Conceptualization, Investigation, Methodology, Software, Formal analysis, Visualization, Validation, Writing - Original Draft, Writing - Review & Editing; **Phillip Gräfensteiner:** Conceptualization, Software, Validation, Writing - Original Draft, Writing - Review & Editing; **Lukas Rubacek:** Supervision, Writing - Review & Editing, Funding acquisition; **Matthias Neumann:** Software, Supervision, Writing - Review & Editing; **Volker Schmidt:** Supervision, Writing - Review & Editing, Funding acquisition; **Thomas Carraro:** Conceptualization, Supervision, Writing - Original Draft, Writing - Review & Editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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1181 Appendix A Derivation details of homogenized equations

1182 Starting from the generic boundary-value problem in Eq. (17), we derive its asymp-
 1183 totic limit in the periodically two-phase microstructure illustrated schematically in
 1184 Fig. 7. The reference cell Y is decomposed into the two phases β and σ , separated
 1185 by the internal interface Γ . The microscopic phase domains β^ε and σ^ε are obtained
 1186 by periodically repeating the reference cell and scaling it by ε , with their internal
 1187 interface denoted by Γ^ε .

1188 The generic microscopic problem in Eq. (17) is therefore written directly in the
 1189 transport phase as

$$\alpha_t \frac{\partial u^\varepsilon}{\partial t}(x, t) - \nabla \cdot (a(u^\varepsilon(x, t)) \nabla u^\varepsilon(x, t)) = 0, \quad \text{in } \beta^\varepsilon, \quad (\text{A.1a})$$

$$-n \cdot a(u^\varepsilon(x, t)) \nabla u^\varepsilon(x, t) = \varepsilon g(x, t), \quad \text{on } \Gamma^\varepsilon. \quad (\text{A.1b})$$

1190 Here, u^ε resolves the periodic heterogeneity of characteristic length scale $0 < \varepsilon \ll 1$,
 1191 and n denotes the outward unit normal of the transport phase β^ε on the internal
 1192 interface. Furthermore, the interfacial flux is scaled as $\varepsilon g(x, t)$ on Γ^ε , which is the
 1193 standard surface-to-volume scaling: in N dimensions, the cell volume scales as ε^N
 1194 whereas the internal interface area scales as ε^{N-1} , so the factor ε ensures an $O(1)$
 1195 contribution in the macroscopic balance.

1196 The homogenized solution to Eq. (A.1) is obtained formally as $\varepsilon \rightarrow 0$ [32, 33, 38].
 1197 To derive this limit problem, we use the ansatz

$$u^\varepsilon(x, t) = \sum_{i=0}^{\infty} \varepsilon^i u_i(x, y, t), \quad y = \frac{x}{\varepsilon}, \quad (\text{A.2})$$

1198 where the functions $u_i(x, y, t)$ are Y -periodic in the fast variable y . Substituting this
 1199 ansatz into the governing equation, using $\nabla = \nabla_x + \varepsilon^{-1} \nabla_y$, and collecting terms of
 1200 equal order in ε yields the successive problems associated with the homogenization
 1201 procedure. Accordingly, the nonlinear coefficient enters the asymptotic hierarchy
 1202 through its leading-order value $a(u_0(x, y, t))$.

1203 Substituting the asymptotic ansatz into Eq. (A.1a) and collecting terms of equal
 1204 order in ε , as $\varepsilon \rightarrow 0$ gives

$$\begin{aligned} & \varepsilon^{-2} [-\nabla_y \cdot (a(u_0(x, y, t)) \nabla_y u_0(x, y, t))] \\ & + \varepsilon^{-1} [-\nabla_x \cdot (a(u_0(x, y, t)) \nabla_y u_0(x, y, t)) - \nabla_y \cdot (a(u_0(x, y, t)) \nabla_x u_0(x, y, t)) \\ & \quad - \nabla_y \cdot (a(u_0(x, y, t)) \nabla_y u_1(x, y, t))] \\ & + \varepsilon^0 \left[\alpha_t \frac{\partial u_0}{\partial t}(x, y, t) - \nabla_x \cdot (a(u_0(x, y, t)) (\nabla_x u_0(x, y, t) + \nabla_y u_1(x, y, t))) \right. \\ & \quad \left. - \nabla_y \cdot (a(u_0(x, y, t)) (\nabla_x u_1(x, y, t) + \nabla_y u_2(x, y, t))) \right] = 0, \end{aligned} \quad \text{in } \Omega \times \beta. \quad (\text{A.3})$$

1205 and the interface condition is equivalently expanded to

$$\begin{aligned}
& \varepsilon^{-2} [n \cdot a(u_0(x, y, t)) \nabla_y u_0(x, y, t)] \\
& + \varepsilon^{-1} [n \cdot a(u_0(x, y, t)) (\nabla_x u_0(x, y, t) + \nabla_y u_1(x, y, t))] \\
& + \varepsilon^0 [n \cdot a(u_0(x, y, t)) (\nabla_x u_1(x, y, t) + \nabla_y u_2(x, y, t)) + g(x, t)] = 0,
\end{aligned}
\quad \text{on } \Omega \times \Gamma.
\tag{A.4}$$

1206 Equating terms of equal order in ε yields the successive cell problems, and ultimately
 1207 the homogenized problem, as described in the following.

1208 • ε^{-2} **coefficients**

1209 At order ε^{-2} ,

$$\nabla_y \cdot (a(u_0(x, y, t)) \nabla_y u_0(x, y, t)) = 0, \quad \text{in } \Omega \times \beta, \tag{A.5}$$

1210 with

$$n \cdot a(u_0(x, y, t)) \nabla_y u_0(x, y, t) = 0, \quad \text{on } \Omega \times \Gamma. \tag{A.6}$$

1211 Multiplying Eq. (A.5) by $u_0(x, y, t)$ and integrating by parts over the periodic cell
 1212 Y gives

$$\int_{\beta} a(u_0(x, y, t)) |\nabla_y u_0(x, y, t)|^2 dy = 0. \tag{A.7}$$

1213 The boundary term on Γ vanishes by the leading-order interface condition, while
 1214 the contributions on ∂Y cancel pairwise by periodicity. Assuming $a(u_0(x, y, t)) > 0$,
 1215 Eq. (A.7) implies

$$\nabla_y u_0(x, y, t) = 0 \quad \Rightarrow \quad u_0(x, y, t) = u_0(x, t), \quad \text{in } \Omega \times \beta. \tag{A.8}$$

1216 • ε^{-1} **coefficients**

1217 Using $\nabla_y u_0(x, t) = 0$, the order- ε^{-1} coefficients of the domain equation become

$$\nabla_y \cdot (a(u_0(x, t)) (\nabla_x u_0(x, t) + \nabla_y u_1(x, y, t))) = 0, \quad \text{in } \Omega \times \beta, \tag{A.9}$$

1218 with

$$n \cdot a(u_0(x, t)) (\nabla_x u_0(x, t) + \nabla_y u_1(x, y, t)) = 0, \quad \text{on } \Omega \times \Gamma. \tag{A.10}$$

1219 Accordingly, $u_1(x, y, t)$ is linearly dependent on $\nabla_x u_0(x, t)$. Therefore

$$u_1(x, y, t) = \sum_{j=1}^N w_j(y) \partial_{x_j} u_0(x, t) + u'_1(x, t), \tag{A.11}$$

where the y -independent term $u'_1(x, t)$ does not affect the cell gradients. Since $a(u_0(x, t))$ is independent of y and nonzero, substituting Eq. (A.11) into (A.9) and (A.10) the correctors $w_j(y)$ satisfy the auxiliary cell problem

$$\nabla_y \cdot (\nabla_y w_j(y) + e_j) = 0, \quad \text{in } \beta, \quad (\text{A.12a})$$

$$n \cdot (\nabla_y w_j(y) + e_j) = 0, \quad \text{on } \Gamma, \quad (\text{A.12b})$$

$$w_j(y) \text{ is } Y\text{-periodic}, \quad \text{on } \partial Y, \quad (\text{A.12c})$$

$$\int_{\beta} w_j(y) dy = 0. \quad (\text{A.12d})$$

The zero-mean condition here ensures uniqueness of the $w_j(y)$ correctors.

• ε^0 coefficients

Volume averaging the order- ε^0 balance over the periodic cell Y gives

$$\begin{aligned} \alpha_t \frac{|\beta|}{|Y|} \frac{\partial u_0}{\partial t}(x, t) - \frac{1}{|Y|} \int_{\beta} \nabla_x \cdot (a(u_0(x, t))(\nabla_x u_0(x, t) + \nabla_y u_1(x, y, t))) dy \\ - \frac{1}{|Y|} \int_{\beta} \nabla_y \cdot (a(u_0(x, t))(\nabla_x u_1(x, y, t) + \nabla_y u_2(x, y, t))) dy = 0, \end{aligned} \quad \text{in } \Omega. \quad (\text{A.13})$$

Applying the divergence theorem on the latter integral of Eq. (A.13) leads to

$$\begin{aligned} \frac{1}{|Y|} \int_{\partial Y} n \cdot a(u_0(x, t))(\nabla_x u_1(x, y, t) + \nabla_y u_2(x, y, t)) ds_y \\ + \frac{1}{|Y|} \int_{\Gamma} n \cdot a(u_0(x, t))(\nabla_x u_1(x, y, t) + \nabla_y u_2(x, y, t)) ds_y = -\frac{|\Gamma|}{|Y|} g(x, t), \end{aligned} \quad (\text{A.14})$$

in which the integral over ∂Y vanishes because of periodicity on opposite faces of the unit cell, while the integral over Γ is determined by the order- ε^0 interface condition.

Substituting Eq. (A.11) into the remaining cell-averaged transport term gives

$$\frac{1}{|Y|} \int_{\beta} \nabla_x \cdot (a(u_0(x, t))(\nabla_x u_0(x, t) + \nabla_y u_1(x, y, t))) dy = \nabla_x \cdot (A(u_0(x, t)) \nabla_x u_0(x, t)), \quad (\text{A.15})$$

where the effective transport tensor $A(u_0(x, t)) = (a_{i,j}(u_0(x, t)))_{i,j}$ is defined by

$$a_{i,j}(u_0(x, t)) = a(u_0(x, t)) \frac{1}{|Y|} \int_{\beta} (\delta_{i,j} + \partial_{y_i} w_j(y)) dy. \quad (\text{A.16})$$

Thus, the homogenized equation is

$$\alpha_t \frac{|\beta|}{|Y|} \frac{\partial u_0}{\partial t}(x, t) - \nabla \cdot (A(u_0(x, t)) \nabla u_0(x, t)) + \frac{|\Gamma|}{|Y|} g(x, t) = 0, \quad \text{in } \Omega. \quad (\text{A.17})$$

1233 A similar homogenization procedure applies to the electrolyte Eqs. (5) and (6), where
 1234 the flux term is given by $q = k_1(\hat{c}_e(x, t))\nabla\hat{c}_e(x, t) + k_2(\hat{c}_e(x, t))\nabla\hat{\phi}_e(x, t)$. Since the
 1235 derivations presented in this section remain valid for arbitrary linear combinations
 1236 of the transport coefficients k_1 and k_2 , equating the ε^{-1} terms yields analogous
 1237 auxiliary cell problems. Therefore, the corresponding effective transport tensors
 1238 associated with k_1 and k_2 can be obtained from Eq. (A.12), being only dependent
 1239 on the microstructure of the respective domain [38, 39].

1240 Appendix B Simulation domain and mesh convergence study

1241 The geometric symmetry of the benchmark allows the 3D computational domain
 1242 to be reduced. Therefore, as detailed in Section 5.3, one-eighth particle domains,
 1243 shown in Fig. B.20a, are used for a subset of the 3D simulations, with symmetry
 1244 boundary conditions imposed on the cutting planes. To ensure sufficient accuracy, a
 1245 mesh convergence study is performed on a representative P68s particle chunk with
 1246 the A35 additive configuration. As illustrated in Fig. B.20b, five tetrahedral volume
 1247 meshes are considered, ranging from the coarse mesh M1 with approximately 233
 1248 thousand elements to the fine mesh M5 with about 13.7 million elements.

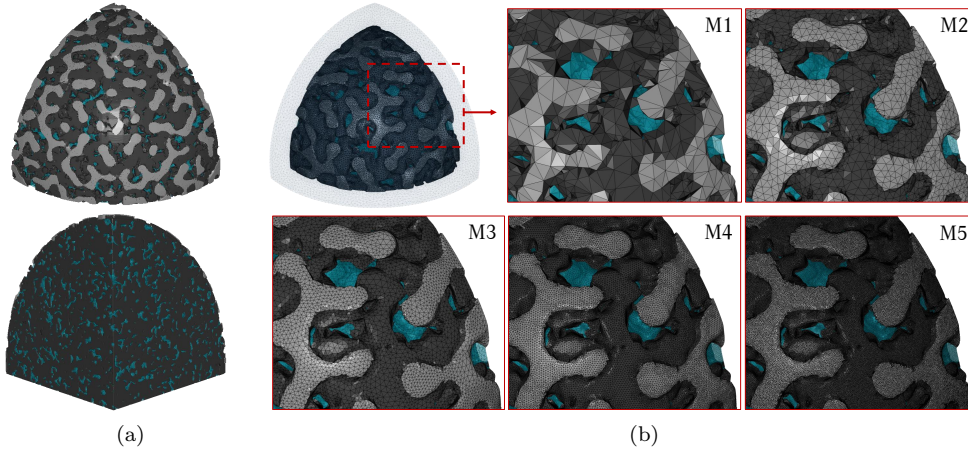


Figure B.20: Computational domain and meshes used for the convergence study. (a) One-eighth chunk of the simulation domain, shown for a P68s particle. (b) Tetrahedral meshes generated for the convergence study based on a P68s porous particle.

1249 Convergence is evaluated using the root-mean-square error (RMSE) of the surface-
 1250 averaged solid potential $\phi_{s,cc}$ relative to the finest mesh M5. Figure B.21 shows a
 1251 rapid decline in RMSE with increasing mesh refinement. Using an RMSE threshold
 1252 of 5 mV as the convergence criterion, the mesh-generation setting for M3, which
 1253 comprises approximately 1.9 million elements and yields an RMSE of 3.1 mV, is
 1254 selected for the subsequent simulations.

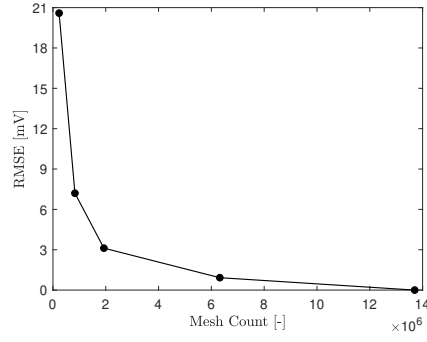


Figure B.21: Root Mean Squared Error (RMSE) of the surface-averaged solid potential $\phi_{s,cc}$, relative to the reference value obtained with the finest mesh (M5) shown in Fig. B.20b.

1255 The selected mesh settings are adopted for the 3D electrochemical simulations and
 1256 for the cell problems used to compute the effective transport tensors.