About the Cover:

The cover art features complexations that underlie a lithium-ion battery porous electrode owing to multimodal interactions including kinetics, transport, and microstructural stochasticity. The manuscript by Mistry et al. highlights the critical role of secondary phase stochastics in long- and short-range interplay and their resulting impact on the electrode properties and performance.
Secondary-Phase Stochastics in Lithium-Ion Battery Electrodes

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ABSTRACT: Lithium-ion battery electrodes exhibit complex interplay among multiple electrochemically coupled transport processes, which rely on the underlying functionality and relative arrangement of different constituent phases. The electrochemically inactive solid phases (e.g., conductive additive and binder, referred to as the secondary phase), while beneficial for improved electronic conductivity and mechanical integrity, may partially block the electrochemically active sites and introduce additional transport resistances in the pore (electrolyte) phase. In this work, the role of mesoscale interactions and inherent stochasticity in porous electrodes is elucidated in the context of short-range (interface) and long-range (transport) characteristics. The electrode microstructure significantly affects kinetically and transport-limiting scenarios and thereby the cell performance. The secondary-phase morphology is also found to strongly influence the microstructure–transport-kinetics interactions. Apropos, strategies have been proposed for performance improvement via electrode microstructural modifications.

KEYWORDS: conductive binder, secondary-phase morphology, porous composite electrode, electrochemically active area, electrode microstructural characterization, Li-ion battery

1. INTRODUCTION

Lithium-ion batteries (LIBs) represent a complex nonlinear system, for which, despite their widespread acceptance, quite a few fundamental questions1−11 still need to be answered to enhance their performance (on volumetric and gravimetric basis), cycle life, and safety. The choice of electrode materials characterizes the theoretical performance bounds, i.e., the thermodynamic limit.15,16 On the other hand, a functioning battery does require other materials such as an electrolyte that ensures cell operation but does not store electrochemical energy.5 Quite interestingly, depending on the three-dimensional arrangement of various phases constituting a typical porous electrode microstructure (active material (AM) accounts for lithium inventory, conductive additive facilitates electron transport in the solid phase, binder provides mechanical connections among active material and conductive additive particles, and electrolyte enables ionic transport), it may be rate limiting.

Electrode preparation as well as specific composition decides the resulting microstructure and in turn cell performance. Various experimental studies carried out in the past decade allude to this intricate correlation among processing stage, performance, and life, but do not probe the electrode microstructure.17−28 Given the empirical nature of these measurements, questions such as which electrode composition gives better performance or improved rate capability cannot be accurately answered. With the advent of three-dimensional imaging techniques, e.g., focused-ion beam scanning electron microscopy and X-ray tomography, many microstructural details of battery electrodes are available.29−38 Such studies suggest that the electrode microstructure is much more complex than that assumed in the otherwise accepted porous electrode theory-based performance model.39−41 The microstructure information obtained through imaging techniques is not readily amenable to electrochemical insights because either only the active material (AM) particle structure is resolved (e.g., X-ray tomography) or a large enough electrode sample cannot be probed (focused-ion beam scanning electron microscopy) or simply because the computational requirements for a simulation resolving vital length scales are enormous.

Because this connection among electrode processing conditions, resulting microstructural features, and electrode operation is quite obscure at the present day, electrode preparation is more of an art rather than a science. For example, many experiments use excess conductive additives or keep porosities too high. The present work presents a comprehensive mathematical study where a composite electrode microstructure is analyzed over a wide range of recipes and drying conditions. A fairly overlooked aspect of LIB electrodes42−46 is the implication of conductive additive + binder phase (secondary solids). (There are a few studies33,47−50 accounting for them, but they neither incorporate secondary-phase...
stochasticity arising from evaporation-driven electrode preparation nor correlate to the electrochemical response of composite electrodes.) The composite electrodes studied here account for different amounts of secondary solids as well as their spatial distribution. The generalized effective property (e.g., tortuosity and active area) relations obtained from microstructural characterization are employed to identify the efficacy of short- and long-range interactions. These microstructural aspects are systematically translated to electrode scale to make performance predictions as well as marginalizes the computational cost. The calculations at different length scales are validated against limiting scenarios to ensure the veracity of predictions and subsequent suggestions.

2. ELECTRODE MICROSTRUCTURE COMPLEXATIONS

Figure 1a shows a composite cathode structure with different solid phases. The AM particles are usually on the order of 1−10 μm, whereas conductive additives are comparatively much smaller (40−50 nm). This difference in the length scale allows one to treat the conductive additive and binder as a joint phase. Also, going toward higher morphologies (i.e., ω → 1) gives rise to a secondary pore network with a smaller pore size in thicker carbon binder domains.

**Figure 1.** (a) Composite cathode for LIBs is made up of multiple phases: AM particles, conductive additives, binder, and voids for ionic transport. (b) Given the order of magnitude difference in length scales of conductive additives and AM, the distribution of conductive additives + binder (referred to as secondary phase or carbon binder domain) can be jointly expressed as a homogeneous phase. (c−e) The microstructure generation procedure outlined here grows the secondary phase with different morphologies varying between a film-type structure (ω = 0) and a fingerlike arrangement (ω = 1). Also, going toward higher morphologies (i.e., ω → 1) gives rise to a secondary pore network with a smaller pore size in thicker carbon binder domains.
properties (especially electronic conductivity) have been measured and reported as a function of the carbon-to-binder ratio. Here, the composite cathodes are generated in two stages. The first stage stochastically produces the AM skeleton, whereas the second stage adds the CBDs. The amounts of both AM and CBDs are calculated from a prescribed electrode composition (weight fractions of solids and porosity). Recently, an experimental study performed by the authors found that for the same composition, the CBD phase distributes differently inside the electrode structure and this secondary-phase arrangement is a strong function of slurry drying conditions, especially the evaporation rate (mesoscale simulations also revealed a similar dependence). These fabricated electrodes with the same composition and porosity exhibit distinct electrochemical response that in turn can only be explained on the basis of different CBD phase arrangements. To emulate different CBD patterns, the secondary-phase addition stage accepts an additional input, \( \omega \), referred to as the morphology parameter because it directly controls the spatial aspects of CBD growth on AM backbone. Qualitatively, the morphology parameter, \( \omega \), is a ratio of CBD’s preference to deposit on predeposited CBD versus an uncovered AM surface. In other words, \( \omega \) can be considered a ratio of the cohesive tendency of CBD to adhesive tendency forming CBD–AM contact and is thus related to interfacial energies of CBD/CBD and CBD/AM interfaces. Smaller values of \( \omega \) describe a CBD phase that has a strong affinity for AM and in turn covers more AM surface by forming a filmlike secondary-phase distribution. On the other extreme, a higher value of the morphology factor gives rise to a tentaclelike CBD phase arrangement, as it has higher selectivity towards the predeposited CBD phase. For the present discussion, the morphology factor is expressed as a normalized value falling in the range 0–1. Therefrom, \( \omega \to 0 \) corresponds to layered deposits, whereas \( \omega \to 1 \) represents more three-dimensional fractal-like growth. These morphological variations are also presented in Figure 1c–e. For these three structures, the AM backbone is identical. The same amount of CBD is added to these microstructures while only varying the morphology factor, \( \omega \). The first column presents the \( x \)-mid plane for a representative elementary volume (REV), and the successive columns magnify different locations on this slice to provide a better visual comparison across different morphologies. In addition to the morphological differences hypothesized on the basis of the definition of \( \omega \), another interesting feature is also present. In closed corners, the higher morphologies have a secondary pore network of smaller pores taking shape in the CBD phase. Such an arrangement is expected to introduce additional pore transport resistance (Note that these pores are filled with electrolyte in a cell; hence, pore network resistance correlates to ionic transport resistance). The algorithmic details to produce composite cathode structures are pictorially summarized in Figure 2, whereas associated subtleties like identification of appropriate REVs and spatial resolution for accurate porous media property
calculations are discussed in the Supporting Information (Section S1). The present set of electrode microstructures and corresponding effective property relations are strictly valid for nickel manganese cobalt oxide (NMC) AM particles (proved to be spherical from tomography experiments\textsuperscript{36,42}), acetylene black as a conductive additive, and poly(vinylidene difluoride) as a binder, but the microstructure generation procedure is universally valid as well as the qualitative

<table>
<thead>
<tr>
<th>Effective microstructural property</th>
<th>Expression</th>
<th>Coefficient of determination, $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pore–AM area\textsuperscript{b}</td>
<td>$a_{21} = (-1.8079(1 - \varepsilon_1\varepsilon_2)^2 + 1.4103(1 - \varepsilon_1 + \varepsilon_2^2)) \times 10^{-6}$</td>
<td>0.9981</td>
</tr>
<tr>
<td>AM–secondary-phase area\textsuperscript{b}</td>
<td>$a_{12} = \varepsilon_1(1 - 1.6119\varepsilon_2 - 0.0663\varepsilon_1^2 - 7.4654(1 - \varepsilon_1\varepsilon_2)^2 + 2.3173(1 - \varepsilon_1 + \varepsilon_2^2) - 4.2340)$</td>
<td>0.9341</td>
</tr>
<tr>
<td>total AM surface area\textsuperscript{b}</td>
<td>$a_{1(1+2)} = -3.5932(1 - \varepsilon_1\varepsilon_2)^2 + 4.3319(1 - \varepsilon_1 - \varepsilon_2) - 0.2483$</td>
<td>0.9580</td>
</tr>
<tr>
<td>pore–secondary-phase area\textsuperscript{b}</td>
<td>$a_{20} = \varepsilon_1(1 - 1.8744\varepsilon_2 + 0.0521\omega(-59.5423(1 - \varepsilon_1) + 74.1352(1 - \varepsilon_1) - 10.3652)$</td>
<td>0.9435</td>
</tr>
<tr>
<td>tortuosity</td>
<td>$\tau = (0.6768 - 5.1707\varepsilon_1 + 12.0492\varepsilon_1^2 + 0.5283\varepsilon_2\omega) \times 10^{-6}$</td>
<td>0.7432</td>
</tr>
<tr>
<td>conductivity\textsuperscript{c}</td>
<td>$\sigma = \varepsilon_1(0.1839 - 0.4219\varepsilon_1 + 1.0475\varepsilon_2 - 0.0186\omega)$</td>
<td>0.9900</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Regression analysis helps quantify the functional form of these relationships. \textsuperscript{b}Dimensionless area; divide by the particle radius to obtain in m\textsuperscript{2}/m\textsuperscript{3}. \textsuperscript{c}Normalized conductivity; multiply by secondary-phase conductivity to obtain in S/m; secondary-phase conductivity as a function of the C/B ratio is expressed in Figure S1c, Supporting Information.

Figure 3. Description of electrode microstructural limitations: (a) The reaction blockage quotient $N_r$ quantifies the resistance to an electrochemical reaction on the basis of electrochemically active area. (c) Correspondingly, electrode recipes can be classified into kinetically limited combinations. (b) The pore network resistance quotient, $N_p$, identifies (f) transport-limited electrodes from porosity and tortuosity variations. (g) A joint picture of microstructural limitations based on electrode classification into kinetically limited and transport-limited recipes. (h) The subset of microstructurally efficient (lower resistance) recipes becomes smaller as AM loading is decreased (i.e., secondary-phase amount increases). Note that the results (a), (b), and (e)–(g) are for electrodes with 95% AM loading. (c) The effective electronic conductivity of most of the electrode composition is better than the corresponding effective ionic conductivity, thus leading to negligible electron conduction limitation, save for a few critical combinations; the values reported here are for $\omega = 1$, i.e., lowest conductive morphology for the same amount of secondary phase. (d) The conductivity trends predicted from microstructural simulations match quite well with equivalent experimental measurements (Liu, G., et al. J. Electrochem. Soc. 2012, 159 (3), A214).
understanding of effective property and electrode performance trends. Note that the secondary-phase arrangement results from the electrode preparation stage because the electrode microstructure is finalized at the end of drying. Henceforth, electrolyte addition does not alter the secondary-phase morphology. Sometimes it is observed that electrolyte is absorbed by the binder phase in excess quantities and leads to swelling of the CBD phase. This swelling physics is not considered here for the sake of simplicity.

Multiple composite cathode realizations are generated to map the different combinations of weight fractions, electrode porosity, and CBD morphology. Each of these structures is analyzed to quantify the interfacial area (pore–AM, AM–CBD, and pore–CBD), pore phase tortuosity, and the effective electronic conductivity (in all three coordinate directions). The resultant data set is studied to understand the trends in effective microstructural properties. Regression analysis expresses these effective properties as a function of the electrode recipe (Table 1). These functional forms (Table 1) reveal that the correlations are quite involved compared to traditionally assumed forms, e.g., the Bruggeman relation for tortuosity. This is expected because the conventional relations for tortuosity and active area are strictly valid for a granular microstructure made up of nonoverlapping monodispersed spheres, whereas the composite cathodes for LIBs have appreciable amounts of the secondary solids. Moreover, for higher AM loading, the spherical particles overlap and the microstructure departs further from the traditional assumption (The details of effective property calculations are available in Sections S2–S4, Supporting Information. Also, the limits of traditional relations are discussed therein).

Different microstructural properties affect transport processes that govern the cell behavior, thus in turn, dictating the electrochemical operation. For instance, the electrochemically active area is responsible for providing reaction sites for intercalation to take place. Effective electronic conductivity quantifies the ease of electronic conduction, whereas pore phase tortuosity is an indicator of pore network resistance experienced by ionic conduction in the electrolyte phase. To express microstructural effects on these different transport modes, two dimensionless quantifiers are identified: reaction blockage quotient \( N_r \) and pore network resistance quotient \( N_p \) (eqs 1 and 2). As the amount of CBD increases in the electrode recipe, it covers more AM surface and effectively reduces the interfacial area available for the intercalation reaction. This negatively affects the electrochemical reaction. Here, \( a \) is the active area of a given composite cathode, whereas \( a_0 \) is the corresponding active area of the equivalent nonoverlapping spherical particulate structure. Therefrom, \( N_r \rightarrow 1 \) quantifies increased reaction resistance. Similarly, the ratio of porosity (\( \varepsilon \)) to tortuosity (\( \tau \)) expresses the effectiveness of ionic transport. Following the same concept as \( N_r \), \( N_p \) describes the pore phase transport resistance. As \( N_p \) approaches 1, pore phase transport resistance becomes severe.

\[
N_r = 1 - (a/a_0)
\]

\[
N_p = 1 - (\varepsilon/\tau)
\]

(1)

(2)

Note that the electrochemically active area is related to the AM–pore interface. For an electrochemical reaction to take place, one requires AM that could accept Li, contact with the electrolyte to have sufficient Li\(^+\) as well as the presence of ample electrons. In addition, the spread in cell resistance data for same porosity and different AM loading electrodes can only be explained if the pore–AM interface is treated as electrochemically active (Section S7 in the Supporting Information provides the necessary logical support). In other words, Li intercalation can take place only at the pore–AM interface, as the pore–CBD interface blocks Li\(^+\) flux. Thus, the electrochemically active interface is the pore–AM surface. Figure 3a,b sketches the dependence of \( N_r \) and \( N_p \) on porosity and CBD morphology for a fixed AM weight fraction (95% by weight). As expected, the electrode becomes favorable to electrochemical reactions at higher morphologies, i.e., \( \omega \rightarrow 1 \) (Figure 3a). In addition, as the porosity increases from 20 to 40% (by volume) more interfacial area is available, and in turn, \( N_r \) decreases. Given this strong dependence on both electrode porosity and CBD morphology, the different electrodes presented in Figure 3a can be categorized into two regimes (Figure 3e) to identify the kinetically limiting recipes. Note that these trends are for 95% AM (by weight), and qualitatively similar maps can be plotted for other AM loadings. Examine Figure 3b, which describes a similar dependence for pore network resistance \( N_p \). As expected, higher electrode porosity leads to a smaller pore network resistance. An interesting trend is observed here. Higher morphologies (\( \omega \rightarrow 1 \)) give rise to greater pore network resistance. Higher morphologies generate a tentacle-like CBD phase, which protrudes more in the pore phase and effectively creates more hindrance. Moreover, the secondary pore network (as identified in Figure 1d,e) is present in greater quantity. This pore network, given its smaller pore size, offers more resistance. Thus, these two effects lead to a higher tortuosity as CBD morphology is increased and present higher pore network resistance, \( N_p \). The pore network resistance map (Figure 3b), \( N_p \) helps classify the electrodes into transport limiting and nonlimiting recipes (Figure 3f).

Qualitatively similar trends are experienced at different AM loading. Combining the kinetically and transport-limited regions (Figure 3e,f), a comprehensive picture emerges for microstructural resistances of electrodes with 95% AM (Figure 3g). Note that both the limitations do not necessarily occur simultaneously. For lower porosities and lower morphologies, the electrodes are both kinetically and transport limited but there is a window of higher morphologies at lower porosities where the electrodes are not kinetically limited and equivalently, a subset of smaller morphologies at higher porosities reveals that the electrodes are not transported limited. This is quite intriguing because it allows one to fine-tune electrode structures for the kinetically and transport-limited operations separately. To express it differently, the functionality of the electrodes can be directly correlated to operational requirements. Figure 3h explores the effect of AM loading in terms of the resistance classifier diagram (Figure 3g). As AM loading decreases, the CBD amount for the same porosity increases, thus leading to a successively increasing reaction blockage. This expands the kinetically limited recipe toward higher morphologies (\( \omega \rightarrow 1 \)). Another peculiar direction is apparent here. With decreasing AM loading, lower porosities also become accessible. To explain this, consider that the CBD phase is relatively amorphous in comparison to AM (because the CBD phase morphological features have a smaller length scale compared to that of AM particles). Therefrom, increasing the amount of CBD phase leads to a part of the AM volume being replaced by a relatively amorphous CBD phase, which in turn exhibits smaller tortuosity. Note that these maps of different resistances...
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Figure 4. (a) Comparison of experimental results and predictions from pseudo-DNS model shows that the simulations match quite accurately with measurements for 25 μm thick electrode samples over a range of discharge rates. A slight mismatch in the qualitative nature toward the end of discharge is expected to be a result of concentration-dependent solid-state diffusivity (the constant value used for present simulations). (b) Rate capability of a baseline cathode (30% porosity, 90 wt % AM, and ω = 0.5) is expressed over eight different C-rates varying over 4 orders of magnitude. The inset figure shows discharge energy as a function of C-rate (normalized using maximum volumetric energy if the cathode were filled with AM alone). (c) Evolution of different components to internal resistance over C-rate range simulated in (b). The inset figure shows that solid-state conductivity limitation is quite negligible because σ_{eff} = 12.142161 S/m for this recipe and equivalently electron conduction is quite efficient compared with electrolyte phase transport.

comment on microstructural limitations over REV size, and this understanding is to be upscaled to the electrode volume for a complete picture of physicochemical changes and resistance evolution during the electrochemical operation (discussed later on). Such a description consistently accounts for microstructural multilength scale features, different pore-scale transport processes, and experimentally observable electrochemical response.

The intrinsic ionic conductivity of the electrolyte is around 1 S/m (at a typical salt concentration). Accounting for the porous cathode resistance, the corresponding effective ionic conductivity is on the order of 0.1 S/m (κ_{eff} = μ·ε/τ). A porous electrode gradually changes the identity of charge carriers from ions (i.e., Li^+) to electrons and vice versa, with the total current at any cross section along the thickness direction being constant and the same as the current flowing in the external circuit. Thus, a similar amount of current flows through both the electrolyte-filled pore network (related to ionic conductivity) and the composite solid phase (characterized by electronic conductivity). As long as the effective electronic conductivity of the solid phase is about an order of magnitude higher (i.e., σ_{eff} > 1 S/m), the predominant voltage drop takes place in the electrolyte phase and the solid phase offers comparatively negligible resistance to cell operation. Figure 3c sketches the variation of effective electronic conductivity as a function of electrode porosity and AM loading (wt %). Two lines are identified to mark σ_{eff} = 1 and 10 S/m, respectively. A CBD network made up of film-type deposits (ω = 0) represents better interconnections than a fingerlike structure (ω = 1), thus giving rise to a higher conductivity for film-type deposits. Therefrom, to provide insights into the least-conductive secondary-phase network, Figure 3c demonstrates results for the ω = 1 morphology. The plot shows that except for a narrow band of AM loading and porosity combinations, most of the electrodes have reasonably larger electronic conductivities. Figure 3d compares conductivity predictions based on composite cathode modeling reported here against experimental data. The experiments were performed with nickel cobalt aluminum oxide AM while keeping the same CBD phase constituents. The results reveal that the predictions account for all of the measurements fairly well, thus justifying the truthfulness of composite electrode microstructure results.

3. MICROSTRUCTURE-PERFORMANCE INTERPLAY

The effective microstructure properties obtained here are appropriately integrated into a porous electrode theory-based electrochemical performance model. Special attention is paid to the coupling between the porous electrode and the AM particle. Here, the volumetric current source term at the electrode scale is to be accurately translated to the boundary condition for AM particle dynamics and the electrochemically active area definition becomes critical in conserving Li and Li^+ species fluxes. The mathematical details are presented in Section S6, Supporting Information. Figure 4a presents a comparison of model predictions against experimental discharge measurements for 25 μm thick NMC electrodes. The electrode composition, porosity, particle size, etc., are supplied with the experimental study. Because the morphology is not reported experimentally, ω was tuned to obtain the best fit across a range of C-rates. The suitability of this pseudo-DNS model to make predictions is expressed through this comparison where a reasonable match is obtained over a wide range of C-rates. There appears a slight qualitative mismatch toward the end of discharge at higher rates, and it is authors’ opinion that this arises from concentration-dependent solid-state diffusivity. The present set of electrochemical predictions are with a constant solid-state diffusivity. (The contribution of this concentration overpotential is expected at higher rates, as is evident by Figure 4c.) The electrochemical response of a Li-ion cell is the combination of four transport processes (the ionic transport in the electrolyte phase is closely tied to charge conservation):

1. Li conservation in AM particles
2. Intercalation reaction at the particle–electrolyte interface, representing the change in identity of charge carriers
3. Charge conservation in solid phase (electronic charge—e^-)
4. Charge conservation in electrolyte phase (ionic charges—Li^+ and PF6^-; electrolyte salt is LiPF6).
On the basis of the rate of current flow (i.e., C-rate), each of these processes offers different resistances that jointly manifest as cell internal resistance. To study the evolution of different types of resistances, a thin cathode (25 μm, 30% porosity, 90 wt % AM, ω = 0.5) is studied over a wider range of C-rates: C/5 to 50C. Figure 4b presents the corresponding rate capability simulations. The inset shows the dependence of discharge energy on C-rate. The ideal limit for cell energy in a given electrode volume is it being fully packed with AM and following open circuit potential. This theoretical limit is used to nondimensionalize the discharge energy values in the present work. It can be seen from Figure 4b that at lower discharge rates, the cell voltage approaches that of the open circuit potential (for any electrode composition, cell voltage versus capacity expressed as per unit weight of AM approaches the open circuit potential as the C-rate is decreased; the maximum theoretical energy is achieved when the entire electrode volume is filled with AM and nonintercalating phases are absent, but such an electrode exhibits severe operational limitations), and as the C-rate increases, the cell overpotential increases monotonically, leading to successively lower average voltages as well as discharge capacities. Corresponding discharge energy trends are supplied in the inset image. Because of the composite nature of the porous cathode (i.e., the presence of nonintercalating phases), the discharge energy saturates at less than 100% in the zero C-rate limit (C-rate → 0). Each of the different transport processes leading to electrochemical operation of these electrodes has an associated contribution to the total overpotential (consider eqs 3–6).

Concentration overpotential

\[ \eta_c = \frac{1}{I_{\text{cat}}} \int_{I_{\text{cut}}} \left( U(C'_i) - U(C'_o) \right) \, dx \]  

(3)

Kinetic overpotential

\[ \eta_k = \frac{1}{I_{\text{cat}}} \int_{I_{\text{cut}}} \eta_{\text{Butler-Volmer}} \, dx \]  

(4)

Ohmic drop in solid phase

\[ \eta_s = \Delta \eta_{0-L_{\text{cat}}} \]  

(5)

Ohmic drop in electrolyte phase

\[ \eta_t = \Delta \eta_{0-L_{\text{cat}}} \]  

(6)

Each of these overpotentials is equivalently expressed in terms of internal resistance components, i.e., \( R_{\eta_c}, R_{\eta_k}, R_s, \text{ and } R_t. \) These resistances averaged over the cell operation at each of these C-rates are quantified and expressed in Figure 4c. Because the electrode conductivity for this baseline is large enough (\( \sigma_{\text{eff}}^\text{baseline} = \)), the discharge energy saturates at less than 100% in the zero C-rate limit (C-rate → 0). Each of the different transport processes leading to electrochemical operation of these electrodes has an associated contribution to the total overpotential (consider eqs 3–6).

5C (0.09 V inc.)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Porosity (% vol.)</th>
<th>AM loading (% wt.)</th>
<th>ω</th>
<th>( \rho_{\text{eff}} ) (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>○</td>
<td>30</td>
<td>90</td>
<td>0.5</td>
<td>2.88</td>
</tr>
<tr>
<td>△</td>
<td>30</td>
<td>95</td>
<td>0.5</td>
<td>3.09</td>
</tr>
<tr>
<td>□</td>
<td>25</td>
<td>95</td>
<td>0.5</td>
<td>3.31</td>
</tr>
<tr>
<td>⚫</td>
<td>25</td>
<td>95</td>
<td>1.0</td>
<td>3.31</td>
</tr>
</tbody>
</table>

- (e) and (f) compare effect of morphology on electrode performance
- Effective density is dry electrode density
- All the electrodes have C/B = 1.0 by wt.

Figure 5. Cathode performance can be improved by rational electrode microstructure tuning based on microstructural limitation maps (a). The baseline electrode microstructure is tuned in three stages: (○ → △) the region of lower resistance is expanded by increasing AM loading (△ → □) major contribution to internal resistance is due to kinetic limitation; hence, porosity is decreased, whereas in the nonkinetically limiting microstructural zone (□ → ⚫), the electrode is made kinetically more efficient by making secondary-phase morphology more fingerlike, thus providing higher active area. (b) The corresponding improvements in kinetic resistance are quantified over the range of C-rates. The inset shows equivalent enhancement in discharge energy. (c) This microstructural tuning also improves gravimetric cell performance. The average voltage improves by an order of 0.1 V. (d) Corresponding microstructural specifications are tabulated, along with dry electrode density. (e) and (f) quantitatively explain cell performance improvement by changing secondary-phase morphology (extreme cases are shown). These electrodes have 30% porosity, 95% by weight AM, the carbon-to-binder ratio is kept 1:1 by weight. As secondary-phase distribution changes from film-type (ω = 0.0) to fingerlike (ω = 1.0), kinetic resistance decreases by about 20%, leading to improved cell performance and discharge characteristics.
12.142161 S/m $\gg$ 0.1 S/m), the solid-state conduction resistance is quite negligible (inset in Figure 4c). The electrolyte phase ohmic resistance (related to tortuosity) manifests more strongly for thicker electrodes; hence, the kinetic resistance and diffusional resistance of the AM particles ($R_e$) largely dominate the internal resistance evolution over a range of C-rates for this cathode (Figure 4c). As the C-rate increases, the contribution of kinetic overpotential decreases due to the logarithmic dependence of Butler–Volmer kinetics. On the other hand, the particle concentration gradients become more severe at higher rates, thus leading to an increased contribution from particle resistance (i.e., concentration overpotential). In addition, the electrolyte phase transport resistance (which is often believed to be only responsible for thicker electrodes) also starts playing an important role toward higher C-rates. In conclusion, for a thin electrode, kinetic resistance dominates the internal resistance evolution and should be targeted for performance improvement. These resistance evolution trends are expected to be different for thicker electrodes. A comprehensive study discussing the thin and thick electrodes and suitable microstructural improvements will be reported in a future publication.

From resistance evolution (Figure 4c), it is suggested that reducing kinetic resistance should lead to improved electrode performance. The corresponding electrode is marked on a resistance classifier diagram (Figure 5a). Given the insights obtained from Figure 3, if one increases the AM loading (keeping the same porosity), reduced CBD uncovers more active area. Hence, AM loading is increased from 90 to 95% and it expands the region of lower resistance electrode recipes on the resistance classifier diagram. Next, because the transport resistance is not dominant, porosity can be reduced to pack more AM (Figure 3g reveals that for this morphology, $\omega = 0.5$, the porosity reduction does not make the electrode kinetically limiting). Thus, porosity is reduced from 30 to 25%. Next, to reduce the kinetic resistance further, the secondary-phase morphology is made more fingerlike (from $\omega = 0.5$ to 1.0). These successive microstructural changes are demonstrated on the microstructure resistance map in Figure 5a. A corresponding decrease in kinetic resistance plotted in Figure 5b shows that each of these steps decreases kinetic resistance consistently and improves performance (Figure 5b inset). Comparison of discharge performance (Figure 5b, inset c) between the baseline and final microstructure reveals that the average cell voltage improves by about 0.1 V and discharge energy increases by 12% on an absolute basis (~25% on a relative basis). Each of these intermediate recipes is described in Figure 5d, along with dry electrode density, which reveals that the electrode density also increased consistently, signifying higher AM loading. The intriguing aspect of this electrode microstructural tuning is that without the understanding of the microstructural resistance map (Figure 3g,h), and components of internal resistance for the baseline recipe, one would not know which aspect needs to be improved upon. The steps like reducing porosity may seem counterintuitive, but with the thorough understanding of the electrode dynamics, one can make informed decisions. Figure 5e,f explores the correlation between cell performance and changes in secondary-phase morphology. Without any change in porosity or AM loading, changing the CBD phase pattern from filmlike to finger-type reduces kinetic resistance by about 20%, improves energy by 1.5% on an absolute basis (and ~2.5% on a relative basis), and boosts cell voltage by 0.1 V. Note that these improvements are proposed on the basis of the mathematical understanding of microstructural limitations and should be experimentally verified for completeness. The confidence in the present discourse stems from different sets of comparisons (with experimental data) carried out to ensure the veracity of the microstructure and performance descriptions.

4. CONCLUSIONS

The present investigation probes the intricate relationship between the electrode microstructural arrangement and electrochemical performance for an LIB composite cathode. The nonintercalating solids (conductive additive and binder) exhibit nonlinear effects with respect to electrochemical performance. In small proportions, they ensure sufficient electron conduction and mechanical rigidity but they also reduce the available reaction sites by reducing AM–electrolyte contact when used in excess. In addition, the pore phase transport resistance (which is often expressed in terms of tortuosity) decreases as the CBD phase content is increased. Quite interestingly, the specific arrangement (morphology) of the secondary phase is also found to critically influence various forms of microstructural resistances. Here, short-range (kinetic) and long-range (related to ionic and electronic conduction) resistances are quantified as a function of electrode recipes and joint microstructural limitation maps have been reported.

This accurate microstructural information (in terms of effective properties) is suitably translated to the electrode scale to study the resulting electrochemical response. Electrochemical operation of LIB cathodes is affected by four kinds of overpotentials: kinetic, concentration, and ohmic (in solid and electrolyte phases). They are expressed in terms of resistances to identify C-rate dependence and isolate the dominant limiting transport phenomenon. This understanding of microstructural limitations and evolution of internal resistance components with C-rate opens new avenues for improving cell performance via electrode microstructural modifications. As an example, a thin electrode (for which electrode thickness is of the same order as the REV dimension) is explored for microstructural modifications. From rate capability data on the baseline electrode, it is found that kinetic resistance is the most limiting. Correspondingly, electrode modifications are suggested to reduce kinetic resistance and such changes bring about improvement in electrode performance (i.e., voltage, capacity, energy, and power). Because the studied thin electrodes are kinetically limiting, fingerlike CBD morphologies ($\omega \rightarrow 1$) are favorable. Appropriate controlled experiments should be carried out to compare against these recommendations and identify unresolved physics if any.

|| COMPUTATIONAL METHODS

Finite volume method-based custom routines are developed by the authors to carry out microstructural as well as performance calculations. Relevant details are supplied in the Supporting Information.

| ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b17771.

Microstructure generation (Section S1); effective property calculations, comparison of Bruggeman relation, and regression analysis (Sections S2–S4, Table S1, and Figures S1–S3); effect of AM particle size distribution on
effective properties (Section S5 and Figure S4); electrochemical performance model (Section S6, Table S2, and Figure S5); identification of active area (Section S7 and Figure S6) (PDF)

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Notes

The authors declare no competing financial interest.

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