Investigation of Lithium-Ion Battery Electrode Fabrication Through a Predictive Particle-Scale Model Validated by Experiments

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Investigation of Lithium-Ion Battery Electrode Fabrication Through a Predictive Particle-Scale Model Validated by Experiments

Mojdeh Nikpour

A dissertation submitted to the faculty of Brigham Young University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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ABSTRACT

Investigation of Lithium-Ion Battery Electrode Fabrication Through a Predictive Particle-Scale Model Validated by Experiments

Mojdeh Nikpour
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Doctor of Philosophy

Next-generation batteries with improved microstructure and performance are on their way to meet the market demands for high-energy and power storage systems. Among different types of batteries, Li-ion batteries remain the best choice for their high energy density and long lifetime. There is a constant but slow improvement in Li-ion batteries by developing new materials and fabrication techniques. However, further improvements are still needed to meet government and industry goals for cost, cycling performance, and cell lifetime.

A fundamental understanding of particle-level interactions can shed light on designing new porous electrodes for high-performance batteries. This is a complex problem because electrodes have a multi-component, multi-phase microstructure made through multiple fabrication processes. Each of these processes can affect the final microstructure (particle and pore locations) differently.

This work seeks to understand the porous microstructure evolution of Li-ion electrodes during the drying and calendering fabrication processes by a combination of modeling and experimental approaches. The goal is to understand the mechanisms by which the electrode components and fabrication processes determine the battery microstructure and subsequent cell performance.

A multi-phase smoothed particle (MPSP) model has been developed on a publicly available simulation platform known as LAMMPS. This model was used to simulate particle-level interactions and predict the mechanical and transport properties of four fabricated electrodes. One challenge was to include different electrode components and their interactions and relate them to physical properties like density and viscosity that can be measured experimentally. Another challenge was to generate required electrode property data for model validation, which in general was not found in the literature. Therefore, a series of experiments were conducted to provide that information. Understanding these properties has value to the battery community independent of their use in this study.

The MPSP model helps us explain observed transport heterogeneity after calendering but brings up new questions about the drying process that have not been addressed in previous works. Therefore, the drying fabrication step was studied experimentally in more detail to fill this knowledge gap and explain our simulation results.

The MPSP model can also be used as a predictive tool to explore the design space of Li-ion electrodes where conducting the actual experiments is very challenging. For example, the distinct effect of particle characteristics on electrode transport and mechanical properties are difficult to determine independently, and therefore this model is an ideal tool to understand the effect of these properties. The final model, which is publically available, could be used with adjustments by future workers to test new materials, fabrication processes, or electrode design (e.g., a multi-layered structure).

Keywords: Li-ion battery fabrication, conductivity, tortuosity, microstructure prediction
ACKNOWLEDGEMENTS

God made this work possible, gave me the strength to continue, and invited some intelligent people into this project.

I am most grateful to my adviser, Dr. Dean Wheeler, for his support, encouragement, and constructive advice throughout my academic journey. I appreciate his deep knowledge that he generously shares with all of us as his students. He taught me unbiased and independent thinking.

I would like to give my special thanks to my parents and my brother for their unconditional love and support. They always encourage me to pursue my goals.

I also like to thank Dr. Brian Mazzeo, Dr. David Lignell, Dr. Tommy Knotts, and Dr. Stella Nickerson for their cooperation, comments, and suggestions through my annual evaluations, prospectus, and dissertation.

I am very thankful to get the chance to work with some of the smart students of Brigham Young University including, Nathan Barrett, Zachary Hillman, Baichuan Liu, and Andrea I. Thompson.

This work was partially supported by the U.S. Department of Energy through the Battery Materials Research (BMR) program. I would like to also acknowledge Bryant Polzin of Argonne National Laboratory for providing electrode material for manufacturing and testing.
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1 INTRODUCTION

1.1 Motivation

Renewable energy sources can help minimize carbon emissions. However, they are not always available at a predictable rate and time and therefore not reliable as a principal energy source. As a result, they need to be coupled with an efficient energy storage system to allow time-shifting. Energy storage systems can be in chemical, mechanical, or thermal forms.

Chemical storage systems are generally preferable due to their scalability and geographical flexibility. Li-ion batteries are the most common choice among different chemical storage systems for their relatively high energy density, low rate of self-discharge, and high operational voltage. However, the cost, safety, and capacity fade of these batteries need to be improved for the increasing energy-storage demands.

Conventional electrode fabrication techniques and cell design have not changed drastically since the introduction of Li-ion batteries. Nowadays further improvement is needed and therefore we need a better understanding of the relationship between electrode materials and fabrication processes.

Battery researchers and manufacturers worldwide strive to develop improved materials and fabrication techniques for Li-ion batteries and reduce the cost to produce high-performance porous-composite electrodes. The conventional lithium-ion battery electrode consists of expensive minerals that need to be mined and processed to a high purity. Cell fabrication is a top-down process but it needs to be done precisely so that expensive materials can perform at their utmost
level and the final cell delivers a higher amount of energy over at least an eight-year timeframe for electric vehicles and grid-scale storage applications [1].

The fabrication (the term usually used for small-scale electrode production) or manufacture (large-scale production) of Li-ion batteries consists of different steps: (1) electrode fabrication (mixing, coating, calendering, and slitting), (2) cell assembly (winding and stacking), and (3) battery packaging and formation (packaging, electrolyte adding, formation, degassing and testing) [2]. The focus of this work is the first step where the electrode slurry becomes a porous structure. This structure is the medium for the electrochemical reactions inside the battery. Therefore, the subsequent battery performance and lifetime depend strongly on the porous microstructure of Li-ion electrodes [3].

Even with mature manufacturing techniques, electrode slurry components (active material, conductive carbon, binder, and slurry) are not uniformly distributed. These non-uniformities exist at different length scales. The term heterogeneity in this work is mostly related to mesoscale (5-120 µm) non-uniformities unless otherwise noted.

Some types of heterogeneity are desirable when they facilitate the transport of electrons and ions (e.g., more conductive carbon near the metal substrate favors electron transport or more pores adjacent to the separator can lower the ionic resistivity. But some are harmful (e.g. binder shortage near the metal substrate) leading to microstructure defects that can result in non-uniform current density, temperature, pressure, and cell aging at larger scales (macro-scale heterogeneity) [4].

Studying the random nature of porous electrodes at mesoscale is challenging due to the need to control or predict the particle-level distributions during different fabrication processes.
Therefore, more understanding of fabrication physics through modeling can help researchers design better electrodes with controlled and desirable non-uniformities.

In the remainder of this chapter, there is a discussion of the scope of work and a chapter-by-chapter summary of this document. This is followed by a background section with additional information on Li-ion battery structure and manufacturing, and on previous modeling studies.

1.2 Scope of work

This work sets the goal to provide a fundamental understanding of the relationships between fabrication parameters, microstructure properties, and performance, to develop next-generation Li-ion batteries. This goal is achieved through a combination of simulation and experimental studies. Modeling is necessary especially at the particle scale when quantitative experiments are not easy to conduct.

A predictive model is developed to imitate the fabrication processes and the electrode particle-level interactions. This model seeks the relationship between the fabrication techniques and electrode microstructure heterogeneity sources at micrometer-scale. This is done by combining material properties and fabrication process physics at the same length scale.

The experimental part of this work is conducted to parametrize and validate the model so that the model can be used for any new electrode design prior to the experiments. This simulation-experiment combination generates useful information on the tradeoffs between fabrication parameters and electrode performance.

The mesoscale simulation results are frequently compared to experimental results conducted at larger length and time scales. Therefore, we are dealing with different scales that we
need to connect using an averaging approach over a sufficient and still computationally feasible simulation volume and time when comparing it to experiments done at larger scales. Both simulations and experiments were repeated at least three times to insure the reliability of the collected data. The results were averaged, and a 95% confidence interval was calculated using the student T distribution.

This work consists of three major parts: (1) model development including parameterization and validation (2) investigation of the predictive aspects of the developed model, and (3) complementary experiments supporting and explaining the simulation results.

1.2.1 The MPSP model development and validation

Chapter 2 explains the development of the multi-phase smoothed particle (MPSP) model to simulate the multi-phase, multi-component Li-ion battery electrode manufacturing processes. This model uses fundamental forces and interactions to determine particle dynamics and packing during electrode-fabrication steps. The MPSP model is parameterized and validated by comparison with experimental viscosity, density, electronic conductivity, MacMullin number, and Young’s modulus of electrode films. The MPSP model simulates all major aspects of electrode production: mixing, coating, drying, and calendering, though the focus of this work is on drying and calendering.

Four types of electrodes are included in this study: a graphite anode and three traditional metal oxide cathodes. The model suggests how some types of heterogeneity can form during cathode and anode fabrication. The anode is more susceptible to mesoscale heterogeneities than the cathode due to differences in active particle shape and stiffness.
The model and experiments show that regardless of the active material type, calendering increases the variability in electronic and ionic conductivity due to carbon and binder redistribution. This can be explained by means of the proposed multi-phase packing theory. On the other hand, calendering increases mechanical uniformity as also shown by model and experiment.

This chapter is based on published work titled “Investigating Sources of Li-Ion Battery Electrode Heterogeneity: Part I. Electrode Drying and Calendering Processes” in The Journal of Electrochemical Society [5-8]. The latest version of the MPSP model source codes are available on GitHub [9].

### 1.2.2 Microstructure predictions of the MPSP model

Chapter 3 describes the use of the MPSP model to predict the effects of active material properties on the transport and mechanical properties of the dried and calendered electrodes. The effects of active material particle size, shape, orientation, and stiffness are studied separately for a graphitic anode base case.

The model predicts that smaller active particles produce higher calendered film density, electronic conductivity, MacMullin number, and Young’s modulus, as compared to larger active particles. Some of these are advantageous and some are not, so based on the application the manufacturer can decide which size distribution to use.

The shape and stiffness of active material can also change the mechanical and transport properties of the electrode. Rod-shaped active materials have greater ionic transport and lower
electronic transport compared to the disk and sphere shapes, which have similar transport properties. Increasing the stiffness of the active material increases film porosity and composite Young’s modulus, while lowering electronic transport and increasing ionic transport.

This chapter is based on a manuscript titled “A Model for Investigating Sources of Li-Ion Battery Electrode Heterogeneity – Part 2: Active Material Size, Shape, Orientation, and Stiffness” The Journal of Electrochemical Society, in press [10, 11].

1.2.3 Electrode microstructure evolution during drying

The drying process of electrodes might seem like a simple operation but it has profound effects on microstructure. The modeling work presented in Chapter 2 showed some unexpected particle distribution during drying that needed further investigation. Chapter 4 is an experimental study on the impact of drying rates on electrode phase distribution and transport properties.

First, the pre-dried and dried LCO microstructures are compared using a lab-scale freeze-dryer. The SEM images show apparent differences in the pore and carbon-binder domain structures for the pre-dried and dried electrodes. Then, the effect of the drying condition is further investigated by changing the evaporation temperature for both NMC cathode and graphite anode and studying dried electrodes in terms of microstructure and transport properties.

The spectroscopy results show binder gradients exist in both in- and through-plane directions. Interestingly, the through-plane binder concentration gradient starts to appear at higher temperatures. Furthermore, an optimum drying temperature has been identified, resulting in high electronic conductivity and low ionic resistivity due to a more uniform binder distribution and an
increased adhesion forces. A manuscript based on Chapter 3 is in advanced stages of preparation for submission to a scientific journal [12].

The final chapter of the dissertation summarizes the conclusions drawn from this work and lists some suggestions for future work.

1.3 Background

A better understanding of the relationships between fabrication parameters, microstructure, and performance of the battery can help improve manufacturing parameters and materials. The main purpose of this work is to study the electrode fabrication process by developing a particle-level physics-based model and related experiments. This section discusses the background and related previous works related to Li-ion battery fabrication processes, structure measurements, conductivity, and modeling approaches.

1.3.1 Lithium-ion battery and its manufacturing process

Li-ion batteries (LIBs) are rechargeable, light, and compact batteries with relatively high voltage, energy, and power density, which makes them suitable for portable electronics and electric vehicles (EVs). Light and small lithium ions allow high gravimetric and volumetric capacities and power density [13].

These batteries contain a graphite anode, a lithium metal oxide cathode, an organic electrolyte containing a lithium salt for ionic connection between the two electrodes, and a polymer separator [14]. The contact area of electrodes impacts the power of the cell, and the amount of the active materials determines the maximum energy content of the battery [15].
Figure 1-1 shows a Li-ion circuit diagram. The electrons move from the anode to the cathode through the current collector located on each electrode during discharge. Lithium ions move from the anode to the separator and then to the cathode through the electrolyte. The electrochemical reaction happens when electrons and ions meet on the surface of active particles. The quality of each element and step will determine final cell performance.

![Li-ion Charging and Discharging Circuit Diagram](image)

Figure 1-1. Li-ion Charging and Discharging Circuit Diagram [16].

Understanding the correlations between the fabrication process, microstructure, and battery performance can lead to producing an optimized battery.
1.3.2 Structure measurement

Effective transport parameters, such as diffusivity, and electronic and ionic conductivities, are determined according to the microstructure features (e.g. porosity and tortuosity) that present the pathways for ions and electrons in the porous electrode. Features like tortuosity (the parameter that describes the effect of the electrode morphology on the effective transport properties), surface area, and porosity can be calculated by the spatial distribution of electrode constituents [17].

Some experimental approaches can measure these microstructural features. A combination of focused ion beam (FIB) and scanning electron microscopy (SEM) can be used to examine the three-dimensional microstructure of a porous composite cathode [17, 18]. Wilson et al. [19] analyzed a cathode microstructure and reported irregular shapes with internal cracking. These cracks provide a higher surface area which can lead to more transport paths for ions. However, cracks impact the performance of the battery. They also found out the importance of binders and conductive carbon, which can improve the contact between particles within the small cross-section of the electrode structure.

Experiments have shown that the performance and safety of the battery will improve if the conductive particles are optimally dispersed in the cathode [18, 20]. There is internal resistance variation throughout the electrode film due to mesoscale heterogeneity, which causes non-uniform performance and aging [21, 22].

1.3.3 The conductivity of the electrode

The microstructural features and the particle arrangements affect the conductive properties and subsequent performance of the Li-ion battery [23]. Carbon black can increase the effective electronic conductivity of the electrode. This occurs when the carbon black particles form
pathways between active material particles that facilitate electron mobility. On the other hand, the ionic conductivity increases as more pores exist in the electrode film contacting the electrolyte and providing pathways for ions.

The processes for lowering electronic and ionic resistances generally are competing processes. If the carbon domains become larger, they improve electronic conductivity but also increase the ionic transport resistance. In addition, the calendering process can also affect the electronic and ionic resistances, because in calendering the porosity of a film and the separation distances between particles are decreased. The result is decreased electronic resistance and increased ionic transport resistance which is a result of more tortuous paths for ions to travel through the electrode [24].

Tortuosity has several definitions in the literature. It is used to summarize the difficulty in transport through a structure. Geometrical tortuosity is a dimensionless ionic resistance which is defined as the ratio between the shortest pathways between two points and the straight distance connecting those points. Tortuosity can describe important features of the porous structure like the effective conductivity.

Measuring transport properties is hard because the electrode films are very thin and is even harder to interpret because of the inter-relationships among the effective factors. Therefore, a structural model can be helpful to connect the manufacturing processes to the microstructure features.
1.3.4 Modeling a lithium-ion battery

A model is a mathematical description of a system (e.g. a battery) and numerical simulation is a particular application of that model to predict the response of the system under some specific conditions. The results from the simulation can be used for battery performance assessment or to design a better cell. Li-ion batteries are multiscale, multiphysics systems and modeling the whole system is challenging. Therefore, researchers focus on a single-scale model, then connect different scale models to simulate the overall behavior in multiscale (going from nano or microscale to battery macroscopic response).

Two types of battery models are discussed in this document (Figure 1-2): performance models and structure models. Performance models are designed to simulate the battery behavior considering the electrochemistry of the cell when it is charging or discharging within the working voltage range (~3.6 V). It is computationally expensive to capture all the possible connections among the different processes in an electrochemical cell, so some assumptions are made to simplify the system.

![Figure 1-2. Structure and performance battery models diagram.](image-url)
A pseudo-two-dimensional model was developed by John Newman and co-workers [25] that makes approximations about microstructure by considering transport in two directions: 1) Perpendicular to the current collector for the electrolyte phase. 2) The radial direction of the active material for the solid phase (Figure 1-3). This model provides information about the performance of the batteries based on Li-ion transport and kinetic properties. Material, charge, and energy balances in the electrolyte and solid phases are solved simultaneously with certain initial and boundary conditions using COMSOL.

![Figure 1-3. Schematic of the pseudo-two-dimensional (P2D) model.](image)

In the Newman model, surface reactions and transport-related properties are treated using a volume-averaging technique for solid and electrolyte phases. In volume-averaging, the positions and shapes of all the particles and pores in the electrode are summarized and the properties are averaged over a specific volume. This model assumes that Li ions diffuse in the radial (r) direction of spherical active material. Another assumption is that lithium ions transport through the thickness of the film (normal to current collector) where there is an external force to move the electrons and ions, but not across the other dimensions of the film. These dimensions are large compared to the thickness of the electrode which is less than 100 μm.
Our group [26] developed a P2D model to study the heterogeneity of a Li-ion cell using a combination of a Newman-type and equivalent-circuit model. Electrode heterogeneity is represented as a system consisting of three different regions. Their results indicate the importance of uniformity for ultra-fast charging and long cycle life.

The second category of battery models is the structure models with different length scales that can generate parameters for the Newman-type performance model. Some models are developed within software that can deal with ab initio calculations (e.g. VASP, CRYSTAL, ADF, Gaussian, BigDFT) or with molecular dynamics calculations (e.g. LAMMPS, GROMACS, AMBER). Each of these calculations can be chosen based on the information needed [27]. In this work, a structure model will be developed in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). It is a mesoscale model that simulates the manufacturing processes in a micrometer length scale.

The structure models can be based on random packing of spherical or ellipsoidal particles [28, 29], random seeding and growth of particles [30], or a dynamic collision algorithm [31]. These models reconstruct the electrode structure [32-34]. Other structure models can provide information such as effective conductivity or lithium concentrations by combining the structure models and mechanical models or electrochemistry to study the battery [35-37]. These models can compute the conductivity or concentrations during discharge, without distinguishing among different manufacturing procedures.

Some structure models were developed by prior students at BYU. They are categorized into two groups: stochastic grid (SG) model and dynamic particle packing (DPP) model (Figure 1-2). The SG model generates the electrode structure by swapping voxels (packets of material).
The grid is first a random distribution of material, then the swap processes continue until the simulated structure matches the experimental electrode structure according to equilibrium principles. The SG model is easy to code, but it cannot simulate the change of a real system during a specific period of time. Stephenson et al. [38] used the stochastic grid (SG) model to understand the microstructure and transport properties of lithium-ion electrodes. This approach combines nanoscale carbon, binder, and pores into one domain (called the carbon-binder domain).

The carbon-binder domain (CBD) is different from the active material and micrometer-scale pores, so porous electrodes can be modeled as a three-phase system. Zielke et al. [39] tried two statistical models, a random-cluster model and a fiber model to predict the locations and structure of the CBD.

Fewer people have worked on a discrete element method (DEM) model (which was called dynamic particle packing (DPP) model in our group). This is a particle-based approach where the electrode is simulated by agglomerates of spheres which move under Newton’s laws of motion based on a model for inter-particle forces like Lennard-Jones. Peterson [40] created such 3D microstructure models to study the relationships between electrode microstructure and ionic transport resistance of both Li-ion and alkaline battery cathodes. A combination of experiment and simulation has been used to evaluate the CBD morphology and the effect of electrode composition on transport parameters [41]. Forouzan et al. [42] developed particle dynamics models to relate the fabrication process of a cathode electrode to physical and structural properties using LAMMPS.

The Forouzan et al. model was based on Lennard-Jones interaction model which has attractive and repulsive forces described by potential energies of the particles considering their
positions. This model had some physical deficiencies. They assumed that during the drying step the size of the particles, in a box with periodic boundary conditions, decreases as a result of the higher attraction between particles. They shrank the particles to imitate drying and compared the simulated results to physical and mechanical properties, which shows a good agreement between the model and the experimental data. The main issue with this model was that the liquid part of the simulation acted like gas because of insufficient cohesion or inter-particle attraction. When the interaction forces were adjusted to tune macroscopic properties like viscosity, particles showed gas-like behavior making it impossible to have any interfaces. No coating simulation could be done because of the interface problem. In addition, the solid microstructure was not strong enough under the high stresses of the calendering process that left the calendered structure compact, nonporous, whereas it is expected that the particles resist the pressure exerted by the upper wall. This model was not analyzed in terms of predicting the performance or effective transport properties like conductivity.

Other models have been developed in an attempt to simulate lithium-ion-battery manufacturing [43-47]. They focus on simulating one manufacturing process alone because of all the challenges involved in describing this multi-component, multi-phase interaction series of processes. Even the prior DPP models cannot simulate the whole fabrication process. This drawback motivates further research into an improved DPP model that can simulate the fabrication processes of the electrode.

This work will develop a particle-based microstructure (DPP) model that deals with the manufacturing processes of the battery slurries, with the objectives to improve the simulation of the drying step, assess the performance of the electrode and provide useful information for
Newman-type models. This new model is expected to match the viscosity, show liquid-like behavior (right physics), and simulate the coating, drying, and calendering steps. The proposed model that can handle such conditions is smoothed particle hydrodynamics.
2 THE MPSP MODEL DEVELOPMENT AND VALIDATION

2.1 Introduction

One of the main goals of any manufacturing process is to control product variability. This goal may be achieved by rejecting out-of-specification products. However, such a method provides little feedback on the sources of the problem and can lead to a high volume of costly production waste. A better approach to control variability is to develop a fundamental understanding of the root causes of variability so that improvements can be made to the manufacturing process. The production of lithium-ion batteries has many factors that result in substantial product variability. In this case, fundamental understanding is required on multiple length scales relating to the manufacturing process and includes the arrangement of particles and pores across the electrode that can lead to non-uniform current, temperature, and stress inside the cell.

Attempts have been made to optimize Li-ion battery performance or reduce cost by changes to materials and manufacturing processes. This can include designing more energy-dense materials [13], developing new manufacturing techniques (e.g. microwave drying [48]), or adjusting the conventional manufacturing process while using existing materials. The last approach is often preferred because it is least likely to disrupt a large-scale industrial process. Some prior studies have addressed making better batteries by decreasing the amount of waste [49], reducing the consumed energy, improving the microstructure of the cell [44], or assessing the performance of the cell during exhaustive cycling [50].
In some cases, it may be desirable to add heterogeneity into the electrode structure. For instance, so-called gradient or multi-layered or structured electrodes may have variations in porosity or other properties in the in-plane and through-plane directions [51]. These variations are designed to minimize transport and reaction limitations within thick electrodes.

One of the biggest knowledge gaps in the battery community is the microscopic condition of the mixture of particles during electrode fabrication. The slurry and subsequent film have complicated microstructures composed of multiple components. Because of the high solid content, the slurry and undried film are opaque, and it is difficult to observe heterogeneities. Most studies of microstructure have therefore focused on the dried or pressed electrode film right before cell assembly, or the performance of the cell after assembly, as opposed to studying the film throughout the entire manufacturing process.

This lack of understanding concerning structure formation creates some uncertainties about the manufacturing process. One example is the issue of binder migration during the drying step. It has been proposed that this is a significant problem [52, 53], though there is little evidence of industry attention to this. The hypothesis for such behavior is that as the solvent evaporates, it can carry the binder and the carbon to the surface and away from the current collector. Such redistribution of components across the electrode film could reduce cell performance. Thus, a detailed understanding of structure evolution during fabrication steps can provide needed feedback and inform efforts to improve manufacturing steps.

We seek a unified mesoscale or particle-scale model of the manufacturing process to resolve this knowledge gap, predict structure evolution, and address heterogeneities that are present (and perhaps previously unnoticed) by connecting them to fundamental causes. The goal
is for the model to resolve structure from 1-100 μm lengths and, where possible, to connect results to experimental evidence, including on larger length scales. Heterogeneities in the through-plane direction can be fully resolved by the model. On the other hand, heterogeneities in the in-plane direction can only be resolved to sub-mm lengths. Nevertheless, we hypothesize that larger-scale lateral heterogeneities can be partially caused by phenomena on the shorter length scales which are observable and predicted by the model.

This chapter focuses on the drying and calendering steps of manufacturing. The model shows that calendering causes non-uniform distribution of carbon and binder in the film, in turn affecting local electronic and ionic conductivities. On the other hand, calendering tends to make Young’s modulus more uniform. When such factors can be monitored and managed, we will be able to design more robust electrodes. In a forthcoming chapter using this model, we will additionally show that active material shape, size, and orientation (especially in the case of an anode) contribute to electrode heterogeneity to different extents.

The multi-phase smoothed particle (MPSP) model developed here offers several benefits compared to previous models. The MPSP structure model uses fundamental forces and interactions to determine particle dynamics and packing during electrode-fabrication steps. It is derived from smoothed particle hydrodynamics (SPH), a mesh-free approach to approximate the Navier-Stokes equations for flow problems with widely non-uniform distributions of mass. Our MPSP model uses viscosity as a tuning parameter, a key property of the slurry due to its effect on physical mixing [54], coating [55], and drying [56] steps. Furthermore, the MPSP model can handle the multi-phase nature of the slurry and dried electrode. In addition to offering insight into
manufacturing, the model can predict needed input parameters for Newman-type performance models.

The remainder of this chapter consists of: a brief review of electrode film structure, manufacturing processes, and prior models (Section 2); the modeling approach, explaining the MPSP model in more detail and how it is adapted and parameterized to simulate Li-ion electrode drying and calendering (Section 3); the design of associated experiments (Section 4); and a discussion of experimental and simulated results for heterogeneity observed in composition, conductivity and Young’s modulus of four different electrodes (Section 5).

2.2 The manufacturing process of Li-ion electrodes

Electrode manufacturing processes comprise 47% of Li-ion cell production costs. These processes are only partially optimized and therefore have further potential for cost reduction [55]. Conventional fabrication of lithium-ion electrodes consists of mixing, coating, drying, and calendering steps, as shown in Figure 2-1 and discussed below.

Figure 2-1. Manufacturing processes: (a) mixing, (b) coating and drying (red bars indicate heating elements), and (c) calendering.
Mixing. Components of the electrode (carbon black, binder, and active material) are mixed with a solvent to form a slurry. Adequate mixing involves dispersing small aggregates of active and additive materials uniformly without breaking the particles. Different mixing methods are used to ensure homogeneity such as grinding (to make uniform particle sizes), sonication (to speed up the dissolution of solid particles), or stirring. Appropriate combinations of mixing stages and techniques can prolong the lifetime and enhance the performance of the cell [56, 57].

Coating and Drying. The slurry is coated on a metal foil current collector utilizing a doctor blade, slot die, or other processes to form a uniform film (40-150 μm in thickness). The goal is to coat with less than 2 μm variation in measured thickness, which is best achieved using a slot die [49].

The film is heated to evaporate an organic or aqueous solvent [58] (a relatively slow and high-cost operation). The goal of the drying procedure is to consolidate the materials and to maintain the uniform distribution of the components as the porous structure is evolving [59].

Calendering. The dried film is compressed between metal rollers to increase the volumetric energy density [60], obtain a desired porosity, and improve electronic contacts. The challenge is to avoid over-calendering and forming cracks in the film or in active material particles. Low porosities can also hinder lithium-ion transport, decreasing the cell's rate capability. Typical optimized porosity is around 35% [61].

After these steps, the cathode composite film, anode composite film, separator, electrolyte, electrical connections, and packaging are assembled to make an electrochemical cell [62].

Many factors can affect the electrode structure, including (1) the type, size, shape, and composition of the active material, (2) the type and quantity of carbon and binder particles, (3) the
temperature of the slurry, (4) the sequence of mixing [54], (5) variation in the drying protocol [44], (6) the coating shear rate and thickness, and (7) the degree of calendering [63, 64]. While all the manufacturing steps could also contribute to heterogeneity, this work focuses on studying the structure during drying and calendering.

2.3 Electrode structural features

Electrode microstructure can be assessed in terms of a few physical properties. In general, an efficient electrode with minimum overpotential on the cell level needs to have sufficient ion and electron mobility and stable mechanical properties. Porosity and tortuosity are typically used to summarize or analyze the effect of pore geometry on cell performance. These parameters can be measured by direct experiment or can be estimated based on the spatial distribution of electrode constituents [17]. If transport, reaction, or mechanical properties are heterogeneous, the resulting non-uniform current, voltage, temperature, or stress exacerbate the performance, battery life, or safety issues on a cell level [4, 65].

A combination of focused ion beam (FIB) or broad ion beam (BIB) and scanning electron microscopy (SEM) can be used to examine the three-dimensional microstructure of a porous composite cathode (Figure 2-2) [17]. These images show the heterogeneous cross-section and top views of an uncalendered electrode. The active material and micropores are the most distinguishable phases. For modeling and analysis purposes, we consider aggregates of carbon black additive, binder, and associated nanopores as one phase or a quasi-homogeneous material called the carbon-binder domain (CBD) [38]. Therefore, there are 3 domains: active material, larger pores, and CBD.
Figure 2-2. SEM pictures showing heterogeneity of a dried, uncalendered lithium cobalt oxide (LCO) electrode film: (a) cross-section perpendicular to the current collector, (b) top-view surface parallel to the current collector (20 µm scale bar applies to both).

Internal resistance variation exists throughout the electrode film due to mesoscale heterogeneity which can cause non-uniform performance and aging [22]. Lithium ions move through the electrolyte, meaning that microscale pores have the highest ion transport. Electrons can travel through CBD, and to a greater or lesser degree, active material. The electrochemical reaction happens when ions and electrons meet at the active material.

The microstructural features and particle arrangements affect the conductive properties and subsequent performance of Li-ion batteries [23, 66]. Carbon black can increase the effective electronic conductivity of the electrode by forming pathways between active material particles that facilitate electron mobility. On the other hand, the ionic conductivity increases with the amount of connected pores, particularly those that originate at the separator.
2.4 MPSP Model

The multi-phase smoothed particle (MPSP) model developed in this work aims to reconstruct the 3D electrode microstructure using a form of smoothed particle hydrodynamics (SPH) implemented in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software [67]. Nevertheless, our model has a discrete element method (DEM) flavor, meaning we use the SPH particles in the case of active material to represent actual solid particles and not just a means to smoothly interpolate or locally homogenize material properties.

DEM is a powerful tool and useful in many situations. One of the main disadvantages of DEM observed in our previous DEM manufacturing model is unstable interfaces while otherwise trying to maintain liquid- and solid-type behavior. For instance, a specific problem was getting the viscosity or stiffness right and still having a stable interface.

The SPH model is more directly connected to experimental properties such as viscosity, density, and stiffness. In a sense, this chapter is an experiment to see how well SPH could work in a DEM-type environment. The development, parameterization, and application of the model are discussed in this section.

2.4.1 SPH basis of the model

SPH solves the Navier-Stokes equations for particles by creating a smooth, continuous, mesh-free field from particle quantities (see Appendix). A smoothing kernel with radius $h$ defines a weighting function around each particle, which in turn controls the particle’s effect on its neighbors. This radius needs to be large enough to include a sufficient number of interacting neighbors for stable dynamics while small enough to maintain acceptable computational costs.
Pressure and viscosity depend on the inter-particle interactions. The pressure force is the main cause of attraction and repulsion between neighboring particles.

SPH has some advantages and disadvantages compared to mesh-based methods. Advantages include the ease with which SPH can deal with interfaces, complex geometries, moving or deforming boundaries, and large regions of empty space while conserving mass, energy, and momentum. Computations efficiently occur only at mass locations [68, 69]. SPH can have some difficulties with rigid walls, which are approximated by dense arrays of particles. The particles near the wall can have fewer neighbors, sometimes causing mechanical instabilities and penetration problems through the walls. In this work, the penetration problem is solved by making the wall particles as stiff as possible (though without too much repulsion) and multiple-layered. Secondly, if penetration happens, the sign of the normal velocity component is reversed, causing the penetrating particle to elastically move back to the simulation box.

Even though SPH simulations are designed to handle density variations, our simulations present a special challenge due to the widely dissimilar particle types. The resulting density variations can lead to large pressure fluctuations. This was resolved by careful adjustment of simulation parameters such as the smoothing length $h$ (see Table 1).

### 2.4.2 Adaptation for Li-ion battery electrodes

The MPSP model uses coarse graining to make the model computationally feasible, as shown in Figure 2-3. Each CBD particle is a homogenization of thousands of 50 nm carbon black particles, as well as many polyvinylidene fluoride (PVDF) binder molecules and nanoscale pores. N-Methyl-2-Pyrrolidone (NMP) solvent particles likewise consist of many molecules. The relative
softness of the CBD and solvent particles allows significant volumetric overlap, which is equivalent to filling of the nanopores with solvent.

The initial slurry structure is created as follows. As illustrated in Figure 2-3, active material particles are formed from aggregates of SPH-type particles, making spheres, disks, and rods imitating sizes and shapes observed in SEM imaging of dried films [42]. Active, CBD, and solvent particles are placed on a hexagonal close-packed lattice in a randomized fashion, with multiple particle swaps to imitate mixing. The structure is placed above a rigid sheet of additional particles representing the current collector. Subsequently, relaxation and consolidation of the structure under SPH dynamics generates the initial coated slurry state prior to drying and calendering simulations.

![Figure 2-3](image-url)

Figure 2-3. Different particle diameters and shapes for the MPSP model based on SEM images of the electrodes. The inset shows an example SEM image of LCO active material.

### 2.4.3 Model parameterization

To determine the parameters for the three main particle types, we attempted to reproduce multiple macroscopic experimental properties that depend on the structure of the slurry and
electrode film. Because multiple properties, parameters, and simulations are involved, a sequential and iterative method was developed. For instance, liquid simulations of pure solvent were compared to the experiment first to determine solvent parameters. Then CBD parameters were found by introducing CBD into the system, again matching to an experimental mixture of carbon, binder, and solvent. Finally, the active particles were added, and properties were again compared between simulation and experiment.

Table 2-1. The MPSP model interaction parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol (Unit)</th>
<th>CBD</th>
<th>Solvent</th>
<th>CPG-A12 Anode Active</th>
<th>LCO Cathode Active</th>
<th>NMC Cathode Active</th>
<th>HE5050 Cathode Active</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smoothing length</td>
<td>$h$ (µm)</td>
<td>2.2</td>
<td>3.0</td>
<td>2.7</td>
<td>2.7</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Speed of sound</td>
<td>$c_0$ (m/s)</td>
<td>150</td>
<td>3</td>
<td>200</td>
<td>170</td>
<td>198</td>
<td>198</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$\mu$ (mPa·s)</td>
<td>61.4</td>
<td>1.6</td>
<td>61.4</td>
<td>1030</td>
<td>962</td>
<td>962</td>
</tr>
<tr>
<td>Rest density</td>
<td>$\rho_0$ (g/cm³)</td>
<td>2.5</td>
<td>2.5</td>
<td>2.3</td>
<td>7.2</td>
<td>6.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 1 comprises the final set of input parameters for the MPSP model. The goal was to have each particle parameter be reasonably close to corresponding experimental values when available. However, that was not always achievable due to coarse-graining implicit in the model, numerical stability issues, and the complexities of multi-phase simulations.

The macroscopic film properties of density, viscosity, and Young’s modulus were primarily used to parameterize the model because they represent important functionalities of the electrode and depend on how accurately the model reproduces particle structures. For example, viscosity is a key property when the electrode slurry is mixed and coated [54, 55, 70]. Table 2-2 shows the simulated viscosities for the full electrode slurries, each falling within 10% of the
experimental viscosity value. The Young’s modulus is one indicator of electrode mechanical stability, specifically the microstructure reaction to stress applied during calendering, cell assembly, and cycling [71, 72].

Table 2-2. Experimental and simulated viscosities (mPa⋅s) at 1000 s−1 shear rate for each slurry containing the indicated active material.

<table>
<thead>
<tr>
<th>Slurry viscosity</th>
<th>CPG-A12 Anode</th>
<th>LCO Cathode</th>
<th>NMC Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>124</td>
<td>1093</td>
<td>1025</td>
</tr>
<tr>
<td>Simulated</td>
<td>121</td>
<td>1195</td>
<td>1128</td>
</tr>
</tbody>
</table>

Viscosity was simulated through a non-equilibrium method commonly used in the molecular dynamics community. A deforming wall-free box is constructed through special periodic boundaries. The applied uniform shear rate and average shear stress (the off-diagonal component of the pressure tensor) are combined to determine viscosity [73].

The overall effects of the model input parameters on structure, macroscopic properties, and numerical stability are complicated, but some effects were observed and factored into the parameterization loop. These are briefly discussed here. The smoothing length \( h \) determines the amount of overlap between neighboring particles and must be large enough to generate stable liquid-like behavior. Higher values of the speed of sound in combination with higher smoothing length make a stiffer material, resulting in larger Young's moduli and viscosities (see Appendix). On the other hand, speeds of sound must be set below direct experimental values because experimental speeds of sound would lead to nearly incompressible fluids with stiff dynamics that could not be simulated in the desired time scale. The viscosity input parameter is used in SPH to dissipate mechanical energy for stability purposes and does not completely determine the
computed macroscopic viscosity. The rest density is used in an equation of state to determine attractive and repulsive forces among particles and the overall hydrostatic pressure: if rest density is smaller than the actual density of the fluid the pressure force will be positive, making the particles repel each other, otherwise an attractive force keeps particles together. The rest density was initially set to the respective pure-component density (solvent, CBD, or active material) and was subsequently modified to achieve a weakly compressible slurry. Finally, we note that the pairwise interaction between dissimilar neighboring particles is determined by combining rules between the two particle properties (see Appendix). Codes used in this chapter are available from an archive [9].

### 2.4.4 Manufacturing simulations

The finalized model and initially mixed structures were used to simulate the drying and calendering fabrication processes (Figure 2-4). Each simulation can take 1-72 hours to complete using 12 parallel processors in a cluster.

![Figure 2-4](image)

Figure 2-4. Representative initial and final structures from drying and calendering simulations using the MPSP model. Particle types are indicated by color. Wall particles represent both the current collector and calendering surface.
The MPSP model is designed to accommodate mixing and coating simulations at different levels of detail. In this work mixing and coating were done in a relatively expedited fashion representative of a highly mixed and uniformly applied coating, as described above. The leftmost structure in Figure 2-4 illustrates a resulting coating structure.

*Drying simulations.* In the actual event of drying, evaporation happens in combination with capillary movement and diffusion of solvent molecules through the porous structure. Nevertheless, drying mechanics for battery electrodes are not fully understood yet. In the MPSP model, size- and time-scale limitations require that physical approximations must be used to imitate the drying process. To represent evaporation and transport, liquid particles are strategically deleted from the slurry in a stochastic process over the course of a simulation with 3-5 million timesteps.

In preliminary simulations for the anode, different drying schemes were explored, namely the locations, sequencing, and rapidity of solvent particle deletions. In one scheme, particles were deleted uniformly throughout the film thickness; in another scheme, particles were deleted sequentially from the top to the bottom of the film. A third “percolation” case is described below. In the case of uniform deletion, the resulting sample microstructure was 56% porous, compared to 51% porous for the top-down case and 48% porous for the percolation case. This modest variation in porosity is due to the degree of structural collapse as pores are formed. The electronic conductivity of the structures follows an expected trend with porosity, namely that the conductivity of the uniform case was 64% and of top-down case was 91%, compared to the value of the percolation case.

The focus of this work is to compare different electrode structures manufactured through identical manufacturing processes, therefore results discussed below are all done with one drying scheme. We chose the “percolation” scheme because it seemed most realistic at this stage of model
development. This scheme employs two different considerations for particle deletion: particles deletions are more favorable for particles closer to the upper surface or that are part of larger aggregates or reservoirs of liquid particles. In other words, liquid in larger and more-accessible pores evaporates first, though eventually all liquid particles are deleted as shown in Figure 2-4. This evaporation procedure required significant modification [9] to the built-in LAMMPS particle deletion algorithm.

Calendering simulations. The calendering procedure involves a constant speed compression (1 µm/µs) to a fixed position corresponding to about 30-35% film porosity, and resulting in a maximum stress in the range of 27-390 MPa, depending on the film composition. The wall is then held stationary for an equal amount of time to allow the structure to partially equilibrate. The wall is then raised. It is intended that this process approximates the calendering process as it is conducted in electrode manufacturing. In a preliminary test on one electrode, the resulting structural properties were relatively insensitive to adjustments to the calendering rate and hold time, with changes in film thickness, electronic conductivity, and MacMullin number not being statistically significant at least for a factor of 10 change faster or slower. Corresponding changes in Young’s modulus were statistically significant but nevertheless were small (less than 6%). The problem of the structure collapsing (not adequately resisting the applied pressure) during calendering in the previous DPP model [42] is not observed in the improved the MPSP model as shown in Figure 2-4.

2.4.5 Post-simulation analysis

Additional properties can be derived from structures resulting from the drying and calendering simulations. First, the simulated structure is segmented, then the phases are assigned
conductive properties. Effective ionic and electronic conductivities of the entire film are then determined by finite volume calculations with an iterative solver [38]. A potential difference is imposed across the segmented structure, and the local potential distribution is determined from the conductivity assigned to each voxel. Local currents are summed to get the total current through the structure which can then determines the effective film conductivity [38].

Young’s modulus. The simulated structure is further studied in terms of Young’s modulus. The stress is calculated based on the wall force acting on the microstructure and the electrode area (30×30 μm²). The strain is computed based on the film initial and calendered thicknesses.

Segmentation. The particle geometry from the simulation is segmented into cubic voxels of size 0.4 μm and each is assigned a single representative constituent phase: active, low-density CBD, high-density CBD, or micropore. The reason for two different CBD types is to better account for the effect of compression on CBD electronic and ionic properties. To do this, the interpolated density of each phase is calculated at the center of each voxel in the manner of SPH (Equation A1). A voxel is assigned as active if the active phase density is higher than 1.3 g/cm³ for the graphite anode, 3.3 g/cm³ for the LCO cathode, 3.0 g/cm³ for the NMC cathode and 2.8 g/cm³ for the HE5050 cathode. If that condition is not met, the voxel is assigned as a high-density CBD voxel if the CBD density is higher than 1.1 g/cm³, otherwise it is assigned as low-density CBD if the density is higher than 0.1 g/cm³. If none of these conditions are met, that voxel is assigned as a pore.

Domain conductivities. The domain conductivities given in Table 2-3 are based on experimental values with some adjustment. The CBD and pore ionic and electronic conductivities are the same for the four electrodes irrespective of the active material. Note that ionic
conductivities are proportional to the arbitrary value selected for the electrolyte (i.e. the “pore” value). Conductivities close to, but not quite, zero are indicated in the table—such small values may be based on experiment or are used for numerical stability of the calculations but ultimately do not change the resulting effective conductivities. The electronic conductivity of the CBD was determined by measuring different pellets made of carbon black and PVDF at different densities and measuring the electronic conductivity. Similarly, the ionic conductivity of the CBD is based on prior measurements [74].

Table 2-3. Assigned domain conductivities for segmented voxels to obtain the effective electronic and ionic conductivities of each film. Values indistinguishable from zero are so-indicated.

<table>
<thead>
<tr>
<th>Conductivity type</th>
<th>CBD (mS/cm)</th>
<th>CP-G-A12 (mS/cm)</th>
<th>LCO (mS/cm)</th>
<th>NMC (mS/cm)</th>
<th>HE5050 (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low dens</td>
<td>1500</td>
<td>~0</td>
<td>10000</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>High dens</td>
<td>2700</td>
<td>~0</td>
<td>10</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>Pore</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>1.2</td>
</tr>
<tr>
<td>Active</td>
<td>2.5</td>
<td>1.0</td>
<td>10.0</td>
<td>~0</td>
<td>~0</td>
</tr>
</tbody>
</table>

Density profiles. The simulated structure is further studied in terms of density heterogeneity in the direction perpendicular to the current collector. A 1D truncated Fourier series or transform is a particularly convenient way of smoothing out particle-based density variations (Equation A1) by naturally integrating over the in-plane directions and focusing on the length scale of interest.

Surface area. The surface area of the active material is calculated from the identities of adjacent voxels in the segmented structure. It is normalized by the mass of active material. It does not account for nanoscale roughness, and so could not be compared to experimental surface areas, but can nevertheless allow for comparisons between conditions used in this study.
2.5 Experimental design

2.5.1 Electrode fabrication

Four different active materials with distinguishable features are used in this work: (1) Phillips 66 CPG-A12, which is graphite with some surface treatment; (2) Sigma-Aldrich lithium cobalt oxide (LCO); (3) Toda NMC532 (LiNi0.5Mn0.3Co0.2O2), which is a more popular choice for cathodes because of reduced cobalt; and (4) Toda HE5050, which is a lithium-rich form of NMC (Li1.2Ni0.15Mn0.55Co0.1O2) [75]. Although not being widely considered for commercial cells, HE5050 is used in this study due to its unique morphology and properties compared to the other cathode materials.

<table>
<thead>
<tr>
<th>Electrode name</th>
<th>Active material</th>
<th>Active shape</th>
<th>Active size (µm)</th>
<th>Active (wt%)</th>
<th>Carbon black (wt%)</th>
<th>Binder (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>CPG-A12</td>
<td>Disc</td>
<td>2-15</td>
<td>92</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Cathode1</td>
<td>NMC</td>
<td>Sphere</td>
<td>9</td>
<td>90</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Cathode2</td>
<td>LCO</td>
<td>Sphere</td>
<td>2-15</td>
<td>90</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Cathode3</td>
<td>HE5050</td>
<td>Sphere</td>
<td>2[^76]</td>
<td>92</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

The electrodes were fabricated as follows. Active material and carbon black were ground by a mortar and pestle for 20 minutes to disperse the carbon black evenly among the active material (dry mixing). NMP solvent and PVDF binder were mixed separately for 30 minutes to activate the binder and to have a uniformly dispersed mixture. All the components were then wet-mixed for 20 minutes with an immersion blender (8400 rpm) and over an ice bath to prevent the heating of the slurry and the accompanying evaporation of NMP. The electrodes were coated on a metal foil using a doctor blade. The drying process took place under an IR lamp for 10 minutes at a film temperature of 150-200 °C. The film was calendered at room temperature between two metal
rollers until the desired porosity of 30-35% was obtained. Table 2-4 summarizes the dry electrode compositions used in this work.

### 2.5.2 Electrode property measurements

**Viscosity.** Rheological properties of the solvent and slurries were measured using a stress-controlled rotational rheometer (AR 2000ex, TA Instruments, USA) with a cone/plate geometry (diameter: 60 mm, angle: 15°). A strain rate of 1000 s⁻¹ was used to determine the viscosity.

**Ionic conductivity.** The blocking electrolyte method was used to determine the tortuosity or MacMullin number [77]. The method fits a transmission line model to the frequency-dependent impedance of a symmetric cell with a non-intercalating electrolyte.

The MacMullin number ($N_M$) is given by the ratio of tortuosity ($τ$) to porosity ($ε$), or the ratio of intrinsic electrolyte conductivity ($κ_{\text{int}}$) to effective conductivity of the porous electrode ($κ_{\text{eff}}$):

$$N_M = \frac{τ}{ε} = \frac{κ_{\text{int}}}{κ_{\text{eff}}}$$

(2 − 1)

MacMullin number can be thought of as a dimensionless ionic resistance; the higher the MacMullin number, the more tortuous the ionic pathways are.

**Electronic conductivity.** Two DC methods were used to measure the in-plane electronic conductivity of the delaminated films, as described in prior work [78]. Both methods produce consistent results.

**Young's modulus.** The Young's modulus of an electrode was measured by a standard compression test using an Instron 3345 instrument. The electrodes were cut to size 1.1 cm × 1.1 cm
and stacked. Each stack contained 40-48 electrodes so that strain could be adequately measured. The instrument compressed the stack at a rate of 4.5 mm/min. Each test was repeated 3 times. In analyzing the data, the relatively incompressible current collector of each film was factored out [72].

**Electrode cross-section.** The electrode films were milled using a broad ion beam (IB-19530CP JEOL cross-section polisher) for 2 hours at an ion beam voltage of 5 kV. FEI Helios Nanolab 600 and ThermoScientific Apreo C scanning electron microscopes (SEMs) were used to study the electrode microstructure and elemental distribution (by EDX).

### 2.6 Results and discussion

This work seeks to answer the following questions: (1) What is the degree of spatial variability of each electrode for properties of interest? (2) What are the factors that lead to such heterogeneity? (3) How well can the model predict observed heterogeneity? The MPSP model can help answer the first two questions that would be challenging to answer with experiments alone.

Figure 2-5 shows a cross-section of each of the four electrodes studied in this work, illustrating differences in particle and electrode morphology. In this study, we used identical fabrication steps for each of the four electrodes to limit fabrication as a source of heterogeneity.
We set the ambitious goal of a single model that can (1) describe multiple electrodes with minimal parameter changes, (2) predict changes to those electrodes during both drying and calendering, and (3) semi-quantitatively calculate important properties such as viscosity, density fluctuations, thickness, electronic and ionic conductivities, and Young’s modulus. Viscosity was already discussed in Section 2.4.3; here we discuss the remaining properties for dried and calendered electrodes. The MPSP model’s particle-based parameters do not directly tie to these film properties. Therefore, the results here serve both to validate the model and illustrate the wide range of properties that can be predicted, including properties that are difficult to obtain experimentally.
2.6.1 Electrode composition

Density is one of the main electrode film properties and is related to mass loading and porosity. Here we also consider individual domain densities (e.g. active vs. CBD) to express composition heterogeneity and better understand the effect of manufacturing steps on possible redistribution of particles. Figures 2-6a and 2-6b show predictions of CBD and active densities as functions of through-plane position for three simulation runs with the same parameters and conditions but different initial randomized particle placement. While results are given for the NMC simulations after drying and calendering, they are typical of all four electrodes. As discussed below, there is a sharp density peak for CBD near the current collector after drying and near both interfaces after calendering. As shown in Figure 6a and 6b, the dried structure thickness varies up to 12 µm due to the initial particle positions and the subsequent configuration changes during drying, and such variation decreases significantly after calendering—issues related to thickness variation are discussed more completely in Section 2.6.2. Furthermore, consistent with a recent study [79], these results show that the active distribution is more uniform after calendering in contrast with the CBD distribution. Therefore, the subsequent non-uniformity in the calendered film characteristics are more likely due to the heterogeneous distribution of CBD particles.
Figure 2-6. Domain density variation in the simulated NMC cathode after (a) drying and (b) calendering; (c) fluorine sampling regions on calendered NMC cathode (SEM); (d) thickness variation across the dried LCO cathode (SEM).

The CBD density peak at the current collector could have multiple causes. Prior mesoscale modeling has suggested that there is a stronger bond between the binder and current collector compared to the bond between the binder and active material [80], which can be affected by the temperature during drying [81]. However, in this work, we parameterized the wall particles to not have particularly strong attractive forces to CBD or active particles. Therefore, the enhanced CBD density is most likely due to geometrical factors, namely inefficient packing of relatively large and
stiff active particles near the wall. This leaves gaps that are filled with comparatively smaller and softer CBD particles. This phenomenon, which we are calling “multi-phase packing theory,” is similar to jamming theory [82-84] but for a system with multiple particles that differ in both size and hardness.

Calendering the dried electrode produces a similar CBD density enhancement on the separator side as shown in Figure 2-6b. Again, the CBD (as the smaller and more mobile phase) can rearrange to fill in gaps and create a flat surface near the walls. In addition, substantial thickness variations present in the dried electrode can contribute to CBD density variations after calendering. On the other hand, vertical heterogeneity in active material density is diminished with calendering due to these particles’ relative stiffness, which in turn leads to avoidance of overlap.

Because of the physics and timescale inherent to the MPSP model, it is not able to confirm or disprove the previously mentioned hypothesis that higher binder concentration on the top surface is caused by evaporating solvent transporting the binder there through advection [52, 85]. However, alternative hypotheses that could explain binder enhancement are suggested by the results here, namely that binder mechanically responds to forces generated by rearrangement of the more-rigid active material during drying and calendering steps, leading to enhancement. We hope to address this issue more thoroughly in future work with the aid of additional experimentation combined with the MPSP model.

The simulation prediction of CBD density enhancement at interfaces is semi-quantitatively confirmed by EDX elemental analysis of an electrode cross section (Table 2-5). Fluorine fractions indicate the relative amount of PVDF binder (a major component of CBD) in each rectangular region corresponding to the yellow boxes in Figure 2-6c. The higher fluorine contents near the
upper and lower boundaries of the calendered film are consistent with the CBD density peaks in Figure 2-6b. To make the comparison between experiment and simulation more direct, the final column of Table 2-5 gives the relative number of CBD particles in rectangular regions that are similar in location to those shown in Figure 2-6c. The simulated and experimental results both show a diminished binder content in the middle region though the magnitude of this effect differs. The experiment shows the highest amount of binder at the top while the simulation shows the highest binder amount at the bottom. These results are consistent with other analytic work [86] suggesting the accumulation of CBD at the electrode/separator interface. Intended future experimentation over a larger lateral sampling area would refine the picture presented here, allowing for more exact quantification of the degree of binder variation with vertical position.

Table 2-5. Normalized binder distributions from EDX K-edge fluorine intensity (Exp) and CBD particle count (Sim) for rectangular regions indicated in Figure 2-6c.

<table>
<thead>
<tr>
<th>Region</th>
<th>Exp</th>
<th>Sim</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>1.38</td>
<td>0.94</td>
</tr>
<tr>
<td>Middle</td>
<td>0.43</td>
<td>0.78</td>
</tr>
<tr>
<td>Bottom</td>
<td>1.19</td>
<td>1.28</td>
</tr>
</tbody>
</table>

2.6.2 Film thickness

Drying and calendering produce substantial changes in the film thickness and also affects thickness heterogeneity in the lateral (in-plane) direction. Figure 2-6d illustrates the lateral variation for a cross section of LCO cathode, showing four different thickness values. Figure 2-7a gives experimental and simulation thicknesses for the four different electrodes after drying and
calendering. The experimental thicknesses in Figure 2-7a are determined with a screw-type micrometer and so correspond to a much larger lateral length scale than does Figure 2-6d.

The error bars in Figure 2-7 are based on 95% confidence intervals. Independent measurements are made on multiple film samples or at multiple locations on one film sample. For the simulations, multiple runs were made from differing starting configurations to generate independent samples.

In this study, electrode films were coated at a setpoint thickness of 80 µm. Nevertheless, by the end of the drying process, there are modest differences in the thicknesses of the four dried electrodes in both simulation and experiment (shrinking by up to 45%). The semi-quantitative agreement between simulation and experiment is purely predictive meaning that model parameters were not adjusted to make this match. As shown in Figure 2-7a, the simulations modestly, though consistently, overpredict the electrode thicknesses. For the drying step this can be related to particle settling and lateral slurry spreading that do not take place in the simulation, either due to the short time scale or to periodic boundary conditions, but were nevertheless observed experimentally. These differences are also affected by particle properties and hence the discrepancy varies from one electrode to another.
Figure 2-7. Post-drying and calendering experimental and simulation results for film (a) thickness, (b) electronic conductivity, (c) ionic MacMullin number, and (d) Young’s modulus. Error bars indicate 95% confidence intervals, and in some cases are too small in magnitude to be visible.
The different electrodes, within experimental uncertainties, had similar shrinkage ratios or proportional changes in thickness during drying. Nevertheless, there is a slight and expected trend with solvent amounts, meaning that slurries with a lower solid mass fraction tended to shrink more. In addition, the post-dried anode has a lower thickness value than would be expected. This could be due to the relative softness of the graphite particles compared to cathode active materials.

In the simulations the resulting thicknesses of the calendered films differ because the films had different initial porosities and thicknesses and different viscoelastic responses to the applied force. Likewise, the electrodes exhibited different amounts of relaxation or spring-back after the removal of the applied force, in the range of 18-30\% of the final film thickness.

Film thickness variability (i.e. surface roughness) is an obvious sign of non-uniformity, indicating different mass loadings, different porosities across the electrode, or both. Thickness variability is observed in all the dried electrodes, and to a lesser degree in the calendered electrodes. This variability occurs on particle length scales (Figure 2-6d) as well as larger mm length scales (Figure 2-7a).

Because the experimental error bars in Figure 2-7 in every case are based on a uniform number of samples (namely 4), the error bars are proportional to the standard deviation and can be taken as a relative measure of lateral heterogeneity when comparing electrodes. Thus, between experimental LCO and NMC films, LCO has more thickness variability. This can be due to its more diverse active material shape and size (Figure 2-5) that would change the film's porosity and subsequent thickness. Ultimately, most of the thickness variability is mitigated or dampened during the calendering step when the film loses up to 48\% of its initial dried thickness. (This compaction is higher than the conventional 10-20\% in industry [87]. The high compaction is
required here by the high initial porosity, in turn caused by higher solvent content of the slurries required by our laboratory coating process.) Nevertheless, the trend of LCO having the largest experimental thickness variability remains after calendering. Therefore, we observe that calendering is not able to smooth all the thickness variations initially present in the electrode film.

2.6.3 Electronic conductivity

Continuing our discussion of Figure 2-7b shows the experimental and simulation results for electronic conductivity. Because of the large range of values for this property (dried electrodes are in the range 1-4500 mS/cm), a log scale is used. There is relatively good agreement between experiment and simulation for dried and calendered films. Of note, the anode's electronic conductivity is approximately 30 times higher than those of the LCO and NMC cathodes. This is primarily due to the electronically conductive graphite present in the anode.

HE5050 shows the lowest experimental electronic conductivity which can be the result of the nanopores inside of the secondary active material particles, and lack of good contacts among different phases. It may also be due to the intrinsically low electronic conductivity of the active material as a result of the atomic composition [88]. However, this active material shows the highest relative increase after calendering (180%). This can be explained by the formation of larger aggregates of active material after calendering, which allow for longer conductive pathways in spite of the poor conductivity of the active material.

The formation of aggregates can be quantified in terms of active material surface area, as shown in Table 2-6. A decrease in the normalized surface area of an active material after calendering indicates the formation of aggregates. This phenomenon happens for all the electrodes but more dramatically for HE5050 where the surface area is larger before drying as a result of
smaller active material size and is decreased as the structure is compressed and active materials are in better contact.

Table 2-6. Simulated active material interfacial surface area (m$^2$/g) for dried and calendered electrodes, normalized by active material mass. Nanoscale roughness is not considered and so areas should only be compared within the table and not to experimental values.

<table>
<thead>
<tr>
<th>Active material</th>
<th>Dried</th>
<th>Calendered</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPG-A12 anode</td>
<td>1.13</td>
<td>0.68</td>
</tr>
<tr>
<td>LCO cathode</td>
<td>1.29</td>
<td>1.02</td>
</tr>
<tr>
<td>NMC cathode</td>
<td>1.21</td>
<td>0.87</td>
</tr>
<tr>
<td>HE5050</td>
<td>1.56</td>
<td>0.66</td>
</tr>
</tbody>
</table>

After calendering, the experimental and simulated electronic conductivities increase modestly due to the compaction of the structures, leading to better contact between particles, consistent with prior work by Trembacki et al. [89], Notably, the change is larger for the anode: electronic conductivity experimentally increased 68% for the anode, 15% for the LCO cathode, 39% for the NMC cathode. Four possible effects can account for this difference between anodes and these two cathodes. First, the irregular shape of anode active material (as opposed to more-spherical cathode material) can lengthen and improve contact pathways. Second, as a softer active material, graphite will tend to deform more under particle-to-particle and external forces, causing additional connections to be formed. Third, anodes generally have larger pore sizes before calendering than do cathodes, and large pores would be diminished to a greater degree by the calendering process [90]. Finally, similar to HE5050, CPG-A12 shows greater surface area reduction after calendering than do LCO and NMC cathodes. This indicates the formation of bigger
aggregates that decrease the effective surface area but increase the contact between the inherently conductive active particles resulting in higher electronic conductivity after calendering.

Between the similar NMC and LCO films, LCO has 20% higher conductivity. This is primarily due to the higher intrinsic conductivity of LCO [88]. Nevertheless, the experimental difference between NMC and LCO conductivities is less apparent after calendering.

Interestingly, both experimentally and in simulation, in-plane electronic conductivity shows greater heterogeneity on mm and larger length scales after calendering (shown by the experimental error bars in Figure 2-7b). Such heterogeneity has been observed for multiple electrodes from multiple manufacturers and so appears to be intrinsic to the coating operations used in current electrode manufacturing [91]. Furthermore, a contributing factor is likely interparticle interactions that tend to create some aggregation or demixing of CBD from other phases which are not simply caused by poor slurry mixing or other easily fixed manufacturing defects. While our simulations are not conducted on mm lateral length scales, particle interactions can produce a similar result on the through-plane density variations as observed in Figure 2-6.

### 2.6.4 Ionic resistance

We use MacMullin numbers (Equation 2-1) to quantify the electrode film capability to transport ions through the macro- and nano-sized pores. Figure 2-7c shows the MacMullin number of the experimental and simulated electrodes before and after calendering. The model matches the experiments semi-quantitatively. As expected, the value $N_M$ of the electrodes increases after calendering, due to solids interfering with pore connectivity.
The ionic resistance of the anode is significantly higher than that of the cathodes after both drying and calendering. In other words, ions generally encounter more tortuous paths in the anode compared to the cathodes. This is a corollary to the high electronic conductivity of anodes, meaning that mechanisms that favor electronic pathways tend to disfavor ionic pathways. For instance, the non-spherical shape of anode active material can lengthen and narrow ionic pathways or otherwise change the distribution of pore geometries [92, 93]. Such factors can likewise be the cause of the higher amount of observed experimental variability (error bars in Figure 2-7c) for anode MacMullin number.

Between the two well-known cathode materials LCO and NMC, NMC has a higher ionic resistance in the dried state (by about 30%). It is not clear why this is the case, but it seems to be due to the distribution of particle sizes: our LCO material has a wider range of sizes (2-15 µm), whereas the NMC material has nearly uniform spheres (≈9 µm). We similarly observe that the NMC film has larger-size clusters of CBD than does LCO. It appears that more continuous and less-tortuous pathways are promoted in the LCO case. After calendering, the difference between the two materials is greatly diminished.

The HE5050 cathode has lower ionic resistance than the other cathodes. It appears that the mono-sized and small primary particles of active material for HE5050 creates more uniformly distributed and interconnected pores to favor ion transport [92]. The nano-porosity of the secondary active particles themselves promotes pathways not available in the other materials and is therefore probably the most-relevant mechanism. In fact, for the simulated HE5050 films, in contrast to the other simulated cathodes, it was necessary to give appreciable ionic conductivity to the active material to better match the experimental film MacMullin number.
The ionic resistance of a calendered electrode is more variable than for the dried state but the effect is not as dramatic as with electronic conductivity. This could be caused by the same mechanisms previously discussed which include non-uniform spatial distribution of macropores and CBD nano-pores. It is likely that the pores at different locations in the film (bulk vs. top vs. bottom) are affected differently by calendering, resulting in additional heterogeneity.

2.6.5 Young’s modulus

Young’s or elastic modulus \(E\) for particle-based composites depends on the underlying materials, their relative mass fractions, and the arrangement of particles. Figure 2-7d shows the Young’s modulus of the dried and calendered electrodes. These porous films are relatively soft, meaning the composite elasticities in Figure 2-7d are well below the respective values for the active materials themselves (e.g. \(E \approx 16\) GPa for graphite and \(E \approx 175\) GPa for LCO [94]). This suggests that the composite mechanical properties are highly dependent on the stability of particle-to-particle contacts, which in turn depend on particle shape and the CBD content and interactions.

As expected, the anode has a lower value of \(E\) because graphite is a softer material than LCO and other metal oxides. Nevertheless, the value is not as low as one might expect. It has been proposed that the relatively large amount of binder in the anode (see Table 2-4) improves its mechanical stiffness [95] and our simulations confirm this.

As for the cathode films, LCO and NMC show similar elasticity and likewise have the same amount of carbon and binder content. In contrast, the HE5050 film has a higher \(E\) value than does NMC. This appears to be almost entirely due to the different morphology of the particles, especially considering that the HE5050 film has a lower CBD content. The model predicts this difference in elasticity quite well even while all the cathodic active materials have nearly the same
mechanical stiffness (as indicated by the speed of sound, see Table 2-1). The smaller active particle of HE5050 has higher surface area and therefore better contact with CBD, which could explain greater cohesion and higher $E$ [96].

Calendering increases the Young’s modulus of all electrodes as a result of shear self-locking phenomenon, causing particles to fit and have closer contact, and has been observed in other fields [96]. This observation can also be related to the multi-phase packing phenomenon described above. The increase in $E$ is more dramatic for the anode (74%) compared to the cathodes (average 45%). This is the result of the interplay between the soft graphite and the higher binder concentration, meaning that there is more opportunity for rearrangement during compression (albeit we should keep in mind that the calendered anode still has a lower $E$ compared to the calendered cathodes).

In contrast with electronic and ionic conductivity, the variability in experimental Young’s modulus (given by the error bars in Figure 2-7d) decreases after calendering. We propose that, under compression, particles with the largest imbalance in forces move the most, leading to a more stable structure in which particles more equally share the applied load and thereby decrease mechanical non-uniformities across the film. For instance, compression evens out the surface roughness and other thickness variations in which particles would be subject to different stress and strain, depending on location. Nevertheless, some variations in $E$ persist because of local variations in the volume fraction of constituent materials, each with their own intrinsic Young’s modulus.

2.7 Conclusion

The MPSP model was developed to explain and predict the physical origins of structure evolution including particle-scale heterogeneities that develop during multiple fabrication
processes. To this end, it has been successful in distinguishing between different types of electrodes in terms of their particle-level descriptors. Nevertheless, perfect agreement between experiment and simulation is challenging because the electrode slurry has a wide range of irregular particle shapes, sizes, and specific interactions that affect the electrode microstructure and properties.

Current top-down production of Li-ion electrodes appears insufficient to produce a uniform microstructure, with this work showing that heterogeneity exists in all four studied electrodes. It is a common belief in the battery world that calendering reduces heterogeneity by smoothing the electrode's surface and eliminating the thickness variations. However, the MPSP model shows that particles are redistributed during calendering such that heterogeneity does not necessarily decrease. Multi-phase packing theory expresses the tendency for a greater fraction of smaller and softer particles to move toward planar, confining surfaces. To summarize, we observe that calendering decreases electrode heterogeneity in thickness and Young’s modulus while increasing electrode heterogeneity in through-plane CBD distribution, electronic conductivity, and ionic conductivity. Even when calendering does create a beneficial reduction in undesired heterogeneity, it does not eliminate it entirely.

Each electrode tested in this work shows distinguishing characteristics in terms of microstructure-related properties: the anode's electronic conductivity and ionic resistance are higher than those of the cathodes due to anode active material non-spherical shape and softness. The LCO cathode has more thickness variability due to its more diverse active material shape and size, with a relatively high amount of thickness variability remaining even after calendering. Between the similar NMC and LCO films, LCO has higher electronic conductivity in the dried
state. The HE5050 cathode shows the lowest experimental electronic conductivity and ionic resistance due to the intrinsically low electronic conductivity of HE5050 active material and the nanopores inside of the secondary active material particles, respectively. Furthermore, HE5050 has higher Young’s modulus than the other electrodes due to its smaller active particle that has higher surface area and therefore better contact with CBD.

In further work, we plan to use the model to further analyze the effects of active material shape, size, orientation, and stiffness on electrode structures and macroscopic properties. These predictions will enable improvement in the design of electrodes and control during manufacturing.

Appendix: SPH modeling

The MPSP model (available for download [9]) is derived from smoothed particle hydrodynamics (SPH). SPH is based on discretization of the integrated Navier-Stokes equations. The fluid is represented by a discrete set of particles that carry velocity, density, and force-field information that define the fluid's distribution of properties by position and time [68].

For any field variable $f$, a local average is calculated by the following equation:

$$ f(r_i) = \sum_j m_j \frac{f_j}{\rho_j} W(|r_i - r_j|) $$  \hspace{1cm} (A1)

where $f(r_i)$ is a smoothed field variable at position $r_i$, $m_j$ is the mass of neighboring particle $j$ that is within a distance of smoothing length, $h$, $W(|r_i - r_j|)$ is the kernel function evaluated at a distance between positions $r_i$ and $r_j$, and $f_j$ and $\rho_j$ are respectively the particle-based field variable and density at position $r_j$.

The core of SPH is the spherically symmetric kernel function that determines the computational speed and stability of the simulation:
\[ W(r) = \frac{105}{16\pi h^3} \left( 1 + 3\frac{r}{h} \right) \left( 1 - \frac{r}{h} \right)^3. \] (A2)

The pressure force is the main cause of attractive and repulsive forces between neighboring particles. A repulsive force distributes densely packed particles to smooth out local density, while an attractive force brings dispersed particles back together. Tait's equation of state determines the pressure as a function of local density:

\[ p(\rho_i) = \frac{c_0^2 \rho_0}{7} \left[ \left( \frac{\rho_i}{\rho_0} \right)^7 - 1 \right] \] (A3)

where \( c_0 \) and \( \rho_0 \) are the speed of sound and density at zero applied stress, respectively. This equation of state is used to model weakly compressible liquids at atmospheric pressure and temperature. The variable \( c_0 \) needs to be adjusted to satisfy the weakly compressible condition without compromising the stability of the simulation [97].

The MPSP model parameters for dissimilar particles are calculated using the following combining rules:

\[ h_{ij} = (h_i + h_j)/2, \quad c_{0ij} = \sqrt{c_{0i}c_{0j}}, \quad \mu_{ij} = (\mu_i + \mu_j)/2 \] (A4)

where indices \( i \) and \( j \) represent particle types (CBD, active material, solvent, wall). The variable \( h_{ij} \) represents the smoothing length, \( c_{0ij} \) represents the speed of sound, and \( \mu_{ij} \) represents the viscosity acting between dissimilar particles.
3 MICROSTRUCTURE PREDICTIONS OF THE MPSP MODEL

3.1 Introduction

Particle and pore distribution non-uniformities in porous Li-ion battery electrodes can lead to variable internal cell resistances as a result of an uneven arrangement of constituent phases [98-102]. For example, local electronic conductivity can decrease in the areas where more pores exist, or local ionic resistance increases if particles form larger agglomerates that make the ionic pathways more tortuous. Therefore, regional material distribution heterogeneity affects regional ionic and electronic transport properties.

To determine such structure-property relationships, how does one determine the microstructure of an electrode? Experimental electrode reconstruction can be destructive (e.g. SEM/FIB) or non-destructive (e.g. X-ray computed tomography) [32, 34, 103]. These 3D reconstructions yield significant insight into structures, especially if done at high resolutions (less than 50 nm). The details of the particle arrangement inside the electrode microstructure can be correlated to other experiments on electrode performance such as electronic conductivity, tortuosity, and surface area. However, 3D reconstruction methods can be expensive, time-consuming, and challenging due to the heterogeneous and multiscale electrode structure. An accurate structure model can bridge the knowledge gap and provide detailed information about the microstructure plus the physics that led to a particular particle arrangement.

Multiple mesoscale or microscale structure models for electrode materials have been proposed in the literature. Electrode reconstructions and predictions have used random packing of
spherical or ellipsoidal particles [28, 29], random seeding and growth of particles [30], or a dynamic collision algorithm [31]. Such methods do not necessarily consider physics implicit in different manufacturing procedures. Other models have been developed with the focus on simulating a single lithium-ion-battery manufacturing step [42-47]. A benefit of such structure models is that they can be combined with transport and kinetic models [35-38] to predict cell performance.

A few years ago our group became motivated to develop a particle-based model that, with a single set of parameters, captures the essential physics of multiple sequential manufacturing processes in order to predict the microstructure of a completed electrode. This is similar in spirit to efforts to develop universal force fields in the molecular dynamics simulation community [104]. Two models have been developed that use fundamental forces and interactions to determine particle dynamics and packing during different electrode fabrication steps [42, 98]. The multiphase smoothed particle (MPSP) model is the more recent and successful one and is introduced in Chapter 2. It is derived from smoothed particle hydrodynamics (SPH) and was carefully parameterized and validated using experimental data.

The model can reproduce and predict different electrode structures resulting from various compositions and active material (AM) types. Based on the predicted structures, one can calculate macroscopic film properties such as conductivities and elastic modulus. To that end, the MPSP model was used to simulate the drying and calendering manufacturing processes for four different electrodes, each with a volume of 30 µm × 30 µm × 80 µm, where the longer dimension is the full film thickness [98]. Films as thick as 150 µm have also been simulated.
The previous model results show the interconnected effect of the manufacturing steps and constituent particle properties on the electrode micrometer-scale variability. For example, calendering can reduce thickness and Young’s modulus variations but it does not necessarily eliminate transport-related heterogeneities. According to the proposed multi-phase packing theory, smaller and softer carbon-binder domains (CBDs) tend to accumulate at the top and bottom confining surfaces.

We observed that the distinct anode and cathode active materials led to different conductive and mechanical characteristics of the dried and calendered films. For example, the graphite anode showed higher electronic conductivity and ionic resistance than those of the tested cathodes due to its inherently conductive, non-spherically-shaped, and relatively soft AMs that preferentially align in a specific direction. Between NMC and LCO active materials, LCO leads to higher cathode electronic conductivity and more variable film thicknesses as a result of more diverse AM shapes and sizes. Finally, the small porous HE5050 AM shows the lowest electronic conductivity and ionic resistance [98].

While the MPSP model was successful in characterizing different types of electrodes, multiple AM particle characteristics were changed at one time and so the unique influence of each characteristic was not finely illuminated. Therefore, this work is designed to better isolate and understand AM particle properties by varying them one at a time. We then assess the effect of particle characteristics on microstructure properties. Additional issues with particle orientation are also considered.

The AM size differences among and within AMs (e.g. 2 µm HE5050 vs. 2-15 µm graphite) motivate the study for the possible effect of particle size on the electrode microstructure evolution
during drying and calendering manufacturing steps. In this work three different size distributions are investigated: uniform large (15 µm), uniform small (4 µm), and poly-dispersed (2-15 µm).

The shape of the active material is another important property. There have been some studies considering new AM shapes [105-108] but there has not been a systematic modeling study of how shape influences the microstructure evolution during manufacturing processes and the subsequent electrode properties that lead to micro-scale heterogeneity. The case studies here are based on three representative AM shapes, namely spheres, disks, and rods.

The rotational asymmetry of irregular (non-spherical) AM can result in anisotropic transport properties of the electrode film. SEM images of graphite anodes show that irregular AM seems to favor a particular orientation during different manufacturing steps (see Figure 3-9 below). One can conceive the possibility that during film coating, particle orientations could be controlled. Therefore, this chapter will study structural evolution for initially oriented AMs and what effect this has on film properties. Three slurries are simulated with horizontal, vertical, and random AM orientations.

Another noticeable difference among electrodes is the elastic modulus. Stiffer electrodes would be expected to have a higher tolerance to applied pressure but with lower fracture resistance. The AM stiffness can directly affect the electrode response to possible stress sources during manufacturing or cell cycling [98, 109]. Two different particle stiffnesses are examined here, roughly corresponding to graphite and a harder form of carbon.

The MPSP model can simulate some aspects of micrometer-scale heterogeneity. One method of assessing the influence of heterogeneity is to repeat simulations with different initial placement of particles. This is indicated by the relative sizes of error bars in the plots below.
Another method also used here is to assess the sensitivity of results to a certain particle property (like size).

The remainder of this chapter consists of a brief review of the electrode materials and their physical properties (section 2), the simulation setup and the experimental design (section 3), and a discussion of results for simulated structures for different particle properties (section 4).

### 3.2 Electrode materials and their morphological properties

Electrodes are made of different AMs with various compositions, shapes, and sizes (Figures 3-1 and 3-2). LiCoO₂ (i.e. LCO) and Li[LiₓMnᵧCo₁₋ₓ₋ₙ]O₂ (i.e. NMC) are the most common cathode AMs due to their layered structures that facilitate ion intercalation/deintercalation [110]. These two AMs are typically spherical with rough surfaces due to secondary particles being formed from smaller primary particles (Figure 3-2); their secondary particle size varies between 2 and 15 µm. Toda HE5050 is a Li-rich NMC (Li₁.₂ Ni₀.₁₅Mn₀.₅₅Co₀.₁O₂) [6] that was previously studied in our work due to its significant difference to other cathode materials, namely small porous spherical particles that are approximately 2 µm in diameter [98]. Graphite is the most-widely-used anode AM [111, 112], and is innately electronically conductive. The baseline particles in this work are intended to imitate CPG-A12 graphite particles, which are non-spherical with a size range of 2-15 µm.

In addition to AM, electrodes are composed of additives such as binder and carbon black to enhance the contact between particles. A binder is typically used to bind different electrode materials together and to the current collector. There are water- and organic-based binders with different chemistries and molecular weights. The molecular weight of binder can impact the slurry viscosity and calendered properties. For example, binders with higher molecular weight increase
the surface roughness due to higher particle agglomeration [113]. Carbon black particles boost the electronic conductivity of the electrode. In this work, properties of the binder and carbon black are embedded in the model in the form of CBD properties like density, volume fraction, viscosity, and phase conductivity. Density for instance affects how attracted CBD particles are to other CBD particles (cohesion) or to dissimilar particles (adhesion).

Both carbon and binder additives decrease the energy density of the cell due to displacing AM volume in the electrode. The additives can also change the transport properties of the film as they tend to form a nanoporous carbon-binder domain (CBD). Therefore, electrode formulation is an optimization problem involving tradeoffs [114]. The goal is to increase the energy density of an electrode without compromising the mechanical and conductive properties of the cell.

Figure 3-1 shows the active material properties of the pure AM powder and the dried graphite anode. The significant non-uniform active particle shape, size, and orientation can be observed in this figure. These factors as well as the particle stiffness (which was proven to be an important analyzing tool in Chapter 1) are studied in this chapter. The amounts of binder and carbon and the manufacturing processes are kept constant to isolate the effect of these AM characteristics.

Note that the model uses a simplified distribution of particle sizes and shapes, namely one shape (at a time) with up to 7 particle sizes. Furthermore, we compare the more realistic particle size distribution to even simpler cases where there is only one particle size, in order to determine the effect of the size distribution.
3.2.1 Particle size

The effect of particle size on microstructure impacts many fields and has therefore received considerable attention in prior work. As a general principle, a range of particle sizes leads to smaller particles filling the gaps formed by larger particles. This increases the electrode mass loading (i.e. total mass over an area or volume) [115]. Smaller particle size increases agglomerate formation [116]. Agglomeration can be understood in terms of attractive forces among particles or the minimization of high-energy exposed surfaces.
A brief summary and analysis of prior work that relates to the four principal electrode manufacturing steps follows.

(1) During mixing, particle size needs to be considered to ensure sufficient mixing. This is due to the effect of particle size on surface energies (particle-to-particle and particle-to-solvent) that can lead to the aforementioned agglomerate formation and non-uniform particle distribution. Generally, smaller particles (AM, carbon, or both) tend to agglomerate more during mixing. Smaller particles also tend to increase the viscosity due to strengthened surface interactions. The goal of mixing is to achieve a homogeneous mixture, which means breaking up the largest agglomerates and thoroughly wetting the components, though the smallest agglomerates are likely less affected [117].

(2) During coating, viscosity and particle agglomeration continue to be important factors. For instance, the presence of particle agglomerates can lead to an uneven coating thickness [49, 55].

(3) During drying, the size of AM can affect the evolution of the electrode porous structure. For example, the small and soft carbon-binder domain (CBD) phase can redistribute near the current collector after drying based on it filling in the gaps between relatively inefficiently packed and stiffer active material, a phenomenon in Chapter 2 we termed multiphase packing theory [98].

The size of the particles can also affect the pore network during drying. Previous studies showed that smaller active particles can create a more connected pore structure in the context of soil systems [108, 118]. A previous study on LiFePO$_4$ cathode active material showed higher electronic conductivity can result from smaller active material [119]. A comparable outcome is predicted from the MPSP model as shown in the results section below.
(4) During calendering, particle size can affect how the electrode microstructure responds to the applied stress. One effect has been described by multi-phase packing theory: the smaller and softer CBD particles develop higher concentrations at the top and bottom surfaces of the electrode during calendering [98]. Another effect concerns elastic modulus and crack formation. The elastic modulus of the electrode is a function of constituent particles stiffness and particle-to-particle contacts. Smaller AM particles are expected to have more cohesive forces due to higher surface areas and increased contacts, leading to higher elastic modulus [96]. While normally a stiffer material would be more susceptible to crack formation, smaller particles have been found to accommodate initial flaws with less propagation of cracks. This is again due to the higher surface area of the smaller particles that can dissipate more internal stresses [120].

Poly-dispersity can affect not only the particle arrangement during electrode manufacturing steps but also cell performance during cycling as a result of particle size impact on the effective capacity and Coulombic efficiency [11, 12]. Such effects can be explained in terms of diffusion and surface reactions in Li-ion batteries. Generally, smaller AMs have smaller diffusion paths and more exposed surface area to intercalation and solid electrolyte interphase (SEI) formation reactions. Increased area means that the kinetic over potential will be less for smaller particles. This in turn will affect the discharge voltage profile where smaller particles favor faster capacity utilization [121]. According to some previous studies [121-123], there is an optimal active particle size specific to the AM type to maximize practical capacity. For example, the optimum size is around 0.5–0.8 µm for a thin-layer LiMn$_2$O$_4$ electrode [123].
3.2.2 Active material shape

The shape of the active material is known to affect the porosity and the inter-connectivity of the particles [108]. Previous studies [124, 125] show that the shape of the particles affects particle positions and alignments when they are suspended in liquid and experiencing shearing flow.

<table>
<thead>
<tr>
<th>NMC532</th>
<th>LCO</th>
<th>HE5050</th>
<th>CPG-A12</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="NMC532" /></td>
<td><img src="image2" alt="LCO" /></td>
<td><img src="image3" alt="HE5050" /></td>
<td><img src="image4" alt="CPG-A12" /></td>
</tr>
<tr>
<td>(~ 9 μm)</td>
<td>(~ 2 - 15 μm)</td>
<td>(~ 2 μm)</td>
<td>(~ 2 - 15 μm)</td>
</tr>
</tbody>
</table>

Figure 3-2. Common cathode and anode active materials with their MPSP model representation (composed of 2 μm spheres) and typical size distributions. CPG-A12 is shown with two different angles to demonstrate the formed disk.

The effect of particle shape has been studied in the context of percolation theory, which seeks to understand the relationship between volume fractions of conducting and non-conducting phases and the resulting conductive paths [126]. Previous studies by Sastry and coworkers showed that a higher aspect ratio of the conductive additive results in a higher electronic conductivity for the composite. They also found that the contact resistance between the active material and current collector is the lowest for spherical shaped AM and highest for the disk-shaped graphite AM; the rod-shaped AM has an intermediate contact resistance [127, 128].
In this study, we study the effect of AM shape on the transport and mechanical properties of the electrode. Figure 3-2 shows spherical- and disk-shaped active particles that could represent common cathode and anode materials and that were included in our prior study [1]. Note that the shapes in this work are idealized shapes composed of aggregates of smaller primary particles. In this work, the effect of particle shape is isolated by holding other parameters such as composition, size, orientation, and stiffness constant. Figure 3-3 shows the different shapes (sphere, disk, and rod), along with their 3D aspect ratios (i.e. height: width: length) that are discussed.

<table>
<thead>
<tr>
<th>Sphere</th>
<th>Disk</th>
<th>Rod</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Sphere Diagram]</td>
<td>![Disk Diagram]</td>
<td>![Rod Diagram]</td>
</tr>
</tbody>
</table>

- $a_1 \approx a_2 \approx a_3$
- $a_1 < a_2 \approx a_3$
- $a_1 \gg a_2 = a_3$

3D aspect ratio
1:1:1 1:4:4 2:1:1

Figure 3-3. Active particle shapes and their 3D aspect ratio studied in this work.

### 3.2.3 Active material orientation

The non-sphericity of AM introduces rotational alignment and an increased tendency for anisotropy. Prior work (in the field of drug delivery, not batteries) suggests that a non-spherical
particle can reorient according to inter-particle and external forces exerted during a particular mechanical process [124]. Similarly, in electrode fabrication, particle alignment can result from particle-to-particle interactions in which adjacent particles adopt similar alignment in order to minimize free volume or potential energy. External forces also can play a role in aligning particles, such as when an electric or magnetic field [129] is exerted on the film or particles are pressed against a flat surface. Therefore, non-spherical particles can be aligned in nonrandom ways, with particle orientation being a function of the rotational inertia, size, and density of the particles as well as any possible external force. These factors vary from particle to particle for Li-ion battery electrodes, which in turn can contribute to electrode-scale heterogeneities causing non-uniform porosity, particle contacts, and the transport properties of the electrode. Furthermore, studies [98, 108, 130] have shown that irregular shapes create more anisotropic tortuosity compared to a symmetrical spherical shape. In other words, even though anisotropy in a composite structure is possible with spherical particles, it is made more likely when particles are non-spherical.

<table>
<thead>
<tr>
<th>Horizontal</th>
<th>Random</th>
<th>Vertical</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Horizontal Orientation" /></td>
<td><img src="image2" alt="Random Orientation" /></td>
<td><img src="image3" alt="Vertical Orientation" /></td>
</tr>
</tbody>
</table>

\[\theta = 0^\circ\] \[\theta = 0 - 90^\circ\] \[\theta = 90^\circ\]

Figure 3-4. Illustration of different orientations of the AM. Note that in the actual simulation there are many more active particles along with solvent and CBD particles present in the slurry.
Many questions remain on the relationships between particle shape and orientation and resulting electrode performance. In this work, we address one possible question, namely whether controlling the orientation of disk-shaped AM can lead to superior electrode properties. Three initial orientation schemes are studied (Figure 3-4). The angle distributions of the disk-shaped AMs are analyzed at each step to determine the degree of particle rearrangements during the drying and calendering processes and how these affect transport and mechanical properties.

### 3.2.4 Active material stiffness

Particle stiffness controls the electrode response to possible stress sources during electrode fabrication or cell cycling. Electrode manufacturing (the focus of this work) involves multiple stress sources especially during calendering that can alter the structure. Stiffer particles exhibit lower plastic deformation and a higher tendency to fracture under possible stresses. Fractures can lead to particle separation affecting the transport properties of the electrode. Our previous study indicated a meaningful difference among the mechanical stabilities of the examined electrodes. Such difference motivates more investigation into the effect of AM stiffness on the dried and calendered microstructures.

Each electrode component has a different stiffness value which can lead to stiffness heterogeneity: (1) carbon black is a relatively stiff particle \((E = 80 \text{ GPa} \ [131])\), (2) polymeric binder is a soft component \((E = 40 \text{ MPa} \ [79])\), and (3) active material can be stiff in the case of metal oxide cathodes \((E = 175 \text{ GPa}) \ [94]\) or soft in the case of graphite anodes \((E = 16 \text{ GPa}) \ [132]\).
3.3 Simulation and experimental procedures

3.3.1 MPSP model

The multi-phase smoothed particle (MPSP) model for predicting 3D electrode microstructure is implemented in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software [67]. The development, parameterization, and application of the model are discussed previously [1]. The simulation source code, input files, and example structures are archived on GitHub [9].

Table 3-1 gives the particle properties for the simulations here, based on the CPG-A12 anode used in the previous study. The simulated dry weight composition is 92% CPG-A12 active material, 6% polyvinylidene fluoride (PVDF), and 2% carbon black. N-methyl-2-pyrrolidone (NMP) is used as the solvent. Anodes made by an aqueous process obviously have different binder and solvent, but the coarse-grained nature of this model (e.g. CBD particles are described in terms of properties in Table 3-1) means it also could be applicable to such systems. The baseline AM case is less stiff, and a stiffer variant AM is given as well. AM particle stiffness is controlled through particle parameters of smoothing length, rest density, and speed of sound as previously discussed [1].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CBD</th>
<th>Solvent</th>
<th>Active baseline</th>
<th>Active stiff</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smoothing length</td>
<td>$h$ (µm)</td>
<td>2.2</td>
<td>3.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Speed of Sound</td>
<td>$c_0$ (m/s)</td>
<td>150</td>
<td>3</td>
<td>200</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$\mu$ (mPa.s)</td>
<td>61.4</td>
<td>1.6</td>
<td>61.4</td>
</tr>
<tr>
<td>Rest density</td>
<td>$\rho_0$ (g/cm$^3$)</td>
<td>2.5</td>
<td>2.5</td>
<td>2.3</td>
</tr>
</tbody>
</table>
3.3.2 Drying and calendering simulations

The drying and calendering simulations are intended to mimic the actual processes. A “network-favored” drying scheme is used for drying in which solvent particles are sequentially deleted to represent the evaporation of the solvent. Preferential deletion happens for particles closer to the upper surface or that are part of larger aggregates or reservoirs of liquid particles. In other words, liquid in larger and more accessible pores evaporates first, and eventually all liquid particles are deleted. One important consideration is due to the timescale difference between simulated and experimental drying that the simulated drying is more conceptual. Specifically, solvent particles are deleted in a particular sequence that imitates but doesn’t precisely correspond to a certain experimental drying rate or temperature.

The calendering procedure involves a constant-speed compression until the film thickness reaches 39 µm resulting in a porosity around 30-35%. The wall is held stationary to allow the structure to equilibrate and then is raised.

The MPSP model used here does not consider cracking internal to the AM particles; though we recognize that this is an important phenomenon for describing the mechanical response to calendering in some cases, and more importantly to lithium intercalation. Such cracking does depend of course on the size, shape, and stiffness of the AM and will affect cell performance [133, 134].

3.3.3 Post-simulation analysis

Mechanical and transport properties can be derived from the structures resulting from the drying and calendering simulations.
**Young's modulus.** The Young’s modulus before and after calendering is determined from the initial and final slopes of the stress-strain curve during the compressive calendering process.

**Segmentation.** In preparation for conductivity and surface area calculations, the particle-based microstructure is mapped onto a grid of cubic voxels of size 0.4 µm. A single representative constituent phase is assigned to each voxel: active, low-density CBD, high-density CBD, or micropore. The reason for the two different CBD types is to better account for the effect of compression on CBD electronic and ionic properties. To do the differentiation, the interpolated SPH particle density of each phase is calculated at the center of each voxel. A voxel is assigned as active if the active phase density is between 1.3-1.9 g/cm$^3$. The active phase density cut-offs are set for each electrode to conserve the mass fractions of AM and CBD before and after calendering. If that condition is not met, the voxel is assigned as a high-density (HD) CBD voxel if the CBD density is higher than 1.1 g/cm$^3$, else it is assigned as low-density (LD) CBD if the density is higher than 0.1 g/cm$^3$. If none of these conditions are met, that voxel is assigned as a pore.

<table>
<thead>
<tr>
<th>Conductivity type</th>
<th>CBD</th>
<th>Pore</th>
<th>Active</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low density</td>
<td>High density</td>
<td></td>
</tr>
<tr>
<td>Electronic (S/cm)</td>
<td>1.5</td>
<td>2.7</td>
<td>~0</td>
</tr>
<tr>
<td>Ionic (S/cm)</td>
<td>0.0025</td>
<td>0.001</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Simulation values of porosity are calculated based on the segmented structure. This overall porosity accounts for the porosity contributed by the pore voxels as well as the nanoporosity contributed by the CBD voxels (55% and 35% porosity for LD and HD respectively). This method...
of calculating porosity is different than the experimental approach of measuring the film thickness and mass.

**Conductivity calculations.** Effective ionic and electronic conductivities of the entire film are then determined by finite volume calculations [38]. An electric potential difference is imposed across the segmented structure, and the local potential distribution is calculated from local conservation of current and the conductivity assigned to each voxel. The total current through the structure then determines the effective film conductivity. The domain conductivities given in Table 3-2 are based on prior experiments [1].

**Surface area.** The surface area between AM and the CBD and pore phases is an indicator of electrochemical accessibility of the AM and also an indicator of the degree of aggregation. Surface areas are calculated from the identities of adjacent voxels in the segmented structure, meaning if two adjacent voxels are of dissimilar phases then this is accumulated as interfacial area. It is normalized by the mass of AM. This calculated surface area does not reflect nanoscale roughness but can provide additional information on particle-to-particle arrangement among different conditions investigated in this study. For instance, if this coarse-grained surface area is reduced, this suggests a larger degree of agglomeration of the active material [118].

**AM angle.** The angle between the short axis \((a_1)\) of disk-shaped AM and the through-plane direction indicates orientation. For the vertical alignment case, this angle is uniformly 90 degrees before drying commences and for the horizontal case, the angle is initially zero. The random case is based on a random angle selection between 0 and 90 degrees. These distributions at the conclusion of the drying and calendering simulations are re-evaluated.
3.3.4 Electrode preparation and cross-section

To produce the images in Figure 3-9, the procedure was as follows. Phillips 66 CPG-A12 AM (92 wt%) and TIMCAL carbon black (2 wt%) were dry-mixed by mortar and pestle for 20 minutes with an intention to break up any aggregates without fracturing particles and disperse the carbon black evenly among the AM. NMP solvent and Kureha 9300 PVDF binder (6 wt% after drying) were mixed separately for 30 minutes to activate the binder and to create a uniformly dispersed mixture. All the components were then wet-mixed for 20 minutes with an immersion blender (8400 rpm) in an ice bath to prevent heating of the slurry and accompanying evaporation of NMP. The electrodes were coated on a metal foil using a doctor blade. The drying process was carried out under an IR lamp for 10 minutes at a film temperature of 150-200 °C. The film was calendered between two metal rollers until a porosity of 30-35% was achieved. For the pre-dried result in Figure 3-9, a separate wet coating was freeze-dried at a temperature of -27 °C under a cold gas stream.

The electrode films were milled using a broad ion beam (IB-19530CP JEOL cross-section polisher) for 2 hours at an ion beam voltage of 5 kV. A FEI Helios Nanolab 600 scanning electrode microscope (SEM) was used to study the electrode microstructure.

3.4 Results and discussion

In this section, the MPSP model is used to make predictions about how various factors create heterogeneity and to explore the parameter space for electrode design. The microstructure properties are assessed in terms of film thickness, porosity, AM surface area, electronic conductivities in the through-plane direction, MacMullin number (ionic resistance) in the through-plane direction, and Young’s modulus.
3.4.1 Active material size

Figure 3-5 shows the cross-sections of simulated microstructures after coating, drying, and calendering for large, mixed, and small disk-shaped active material, plus the physical and transport properties of the dried and calendered films (e.g. film thickness, porosity, AM surface area, electronic conductivity, MacMullin number, and Young’s modulus).

The model predicts the effect of active material size on dried electrode properties. After drying, large AMs function as a structural backbone which can cause higher film thickness and a slightly more porous microstructure (Figures 3-5d and 3-5e). However, the dried MacMullin numbers are similar for all cases suggesting that although the larger case created a slightly more porous structure, the pores are not as interconnected (Figure 3-5h). Based on film thicknesses, small AMs with a higher surface area per volume can cause higher film shrinkage and greater AM agglomeration. Therefore, smaller particles provide more electronic pathways as they form active-active agglomerates. Such more-frequent contacts among small particles were reported by another numerical study [135]. Despite the lower overall porosity, the pore network is still more interconnected for the small-particle case. The mixed case electronic conductivity (Figure 3-5g) is between the other two cases where smaller particles fill the gaps among larger ones creating a higher degree of interconnections compared to the large case. Smaller particles show a higher elastic modulus (Figure 3-5i) after drying and calendering, in agreement with th [98]. A study by Pang et al. on structures of polydisperse coal particles [96] relatedly notes that loose particles, or particles that are not part of the structural backbone, can result in a lower Young’s modulus for the mixture.
Figure 3-5. Simulated cross sections for (a) large, (b) mixed, and (c) small sizes of disk-shaped AM at three stages of coated, dried, and calendered (cal). LD and HD denote high- and low-density CBDs. The simulated dried and calendered (d) film thickness, (e) porosity, (f) AM surface area, (g) electronic conductivity, (h) MacMullin number, and (i) Young’s modulus.
Calendering has a different effect depending on the particle size distribution. As shown in Figure 3-5, the porosity decreases more (26% change) for mixed and small cases compared to the large case (22% change) after calendering. For the smaller particles, calendering pressure leads to further active agglomerate formation as reflected in the surface area decrease, whereas the surface areas for the large and mixed cases remain rather constant. In general, the transport properties of the small and mixed cases are similar after calendering. Between the large and small AM cases, the higher electronic conductivity of the small-sized AM is a reflection of its state of aggregation. Furthermore, the ionic resistance of the large case is lower due to the interconnected pore network.

The results in this section indicate the potential of designing a gradient-type electrode with smaller particles near the current collector (to have higher contacts between the active particles) and larger ones near the separator (to facilitate ion transport). Such a design also could improve utilization of active material across the thickness of the film at higher charge and discharge rates [121].

### 3.4.2 Active material shape

Figure 3-6 shows the effect of AM shapes (randomly oriented disk, sphere, and randomly oriented rod) on electrode properties.

The electrode thickness and porosity after drying provide information on how efficiently particles can pack. Shrinkage ratio or relative change in thickness was highest for disk-shaped AM (29% vs. 24% for sphere and 11% rod). The electrode with rod-shaped particles shrinks less after drying due to the lack of efficient particle packing, i.e. a more open structure for the electrode. Previous studies have shown that rod-shaped particles have lower packing density compared to spherical shapes when packed randomly [136, 137]. This means that rods have fewer contacts and
they are randomly distributed. Prior work has suggested that randomly arranged spheres will pack more efficiently than randomly arranged disks; a similar effect is observed in the drying process here, in terms of the void ratio or porosity [138, 139].

Normally one would expect dried film thickness and porosity to be proportional for a given composition. In this work, that connection is maintained for all cases except for disk vs. sphere in Figure 3-6. The discrepancy is due to the way that overall porosity is estimated, namely by combining the volume of large pores plus a portion of the volumes of the low- and high-density CBD (i.e. due to nanoporosity). Here the disk case has a higher fraction of high-density CBD, with lower nanoporosity, compared to the sphere case.

As-dried results show an interesting difference between the conventional cathode and anode AM. Typically Li-ion cathode materials are spherical and graphite anode materials are more irregular. After drying, the spherical AM particles show higher electronic conductivity associated with higher particle-to-particle connection compared to disk-shaped AM. Relatedly, we observe (Figure 3-6b) that there is a coating of CBD around the sphere-based clusters in contrast to the other cases where CBD form its own clusters. These results indicate that despite the higher electronic conductivity of the graphite anode (because of its intrinsically conductive AM), the typical spherical shape of the cathode AM has the potential to provide more pathways for the electrons. The rod-shaped AM shows the lowest electronic conductivity and MacMullin number as a result of its lower packing density that leads to distinctive higher porosity after drying.
Figure 3-6. Simulated cross sections for (a) disk, (b) sphere, and (c) rod AM shapes. Remainder of the properties (d-i) are the same as those in Figure 4-5.
The elastic modulus of these shapes shows an interesting trend in agreement with the study by Cho et al. [139]. Particle irregularity (non-sphericity) results in a decrease in stiffness. This can be explained by particle rotation and contact slippage for disk and rod shapes that can consume the shear stress. Also, AM irregularity boosts looser packing and therefore a softer network [139].

Calendering has differing effects depending on the active material shape. The primary effect driving electronic conductivity of a composite is the volume fractions of the phases. In the case of rod-shaped active material, its higher porosity means a lower volume fraction of conductive solids and therefore a lower electronic conductivity. Similarly, ionic resistance (MacMullin number) is lower in this case. In all cases, the increased electronic conductivity and ionic resistance after calendering are mostly due to the compression of micropores and nanopores inside the CBD phase.

The relative amounts of low-density and high-density CBD phases change with active material shape and during the calendering step. The volume fractions of the more-conductive high-density (HD) CBD are 2% and 4% for the disk shape, before and after calendering respectively. For the sphere these fractions are 0% and 1%; for the rod shape they are 3% and 3%. These results suggest that calendering compresses the CBD to greater degree for the disk shape. This can explain why the disk-based electrode, which had a lower electronic conductivity before calendering then matches the sphere-based electrode after calendering. For the sphere the majority of the CBD is in the low-density form. As for the rod shape, its electronic conductivity compared to the sphere shape is a relatively constant ratio before and after calendering.

In addition to volume fractions, conductivity of composites is affected by the connectivity or morphology of the most conductive phases, which for electronic conductivity is the active
material in this study. One way to assess the connectivity of the active material is by its surface area; lower surface area means more connections or agglomeration within the active phase and higher surface area means less agglomeration and more connections to pores and CBD. In Figure 6 the most significant point is the relatively high surface area of the disk shape before calendering and the relatively equal amount of surface area for all shapes after calendering. This further explains why the disk-based electrode “catches up” to the sphere-based electrode after calendering, with respect to electronic conductivity. Such a high level of rearrangement for disk shapes upon calendering is in agreement with the experimental study conducted by Dreger et al. [90]. On the other hand, for spherical AM, the calendering pressure acts as a deagglomeration driving force, due to a modest increase in surface area, though the change is not statistically significant.

The disk-based electrode has the highest ionic resistance after calendering even though the value was similar to the other electrodes before calendering. This appears to be caused by the tortuous pathways generated by the disk shape that is further explored below with respect to particle orientation.

During calendering all three electrodes exhibited plastic compressive strain in the range 27-30%. Even though the calendering process attempted to compress each electrode to the same thickness, subsequent relaxation of the microstructure meant that the rod-shaped AM maintained the highest porosity after calendering, and this appears to drive the observed ionic and electronic transport differences from the other electrodes.

3.4.3 Active material alignment

Figure 3-7 presents the angle histograms and averages (over the whole population for one of the three trials) of the disk-shaped AM at the initial, dried, and calendered stages. The model
predicts that drying and calendering make the angles more uniformly distributed and isotropic. Furthermore, calendering produces a notable reorientation toward zero angle (disks lying flat). Nevertheless, particles tend to stay near their initial orientation through both manufacturing processes. Increased variation in angle (less peaked distribution) can cause some variations in electrode properties as detailed in Figure 3-8.

Figure 3-7. Angle histograms of the disk-shaped AM at the initial (pre-dried), dried, and calendered stages. The vertical axis is frequency or probability, arbitrarily scaled. The angle is between the rotational axis of the disk and the film normal axis. The average particle angle and 95% confidence interval are given in the insets.

Figure 3-8g shows that after drying the through-plane electronic conductivities of the dried electrodes vary only slightly for different particle alignment schemes. Initial vertical alignment
creates the highest through-plane electronic conductivity due to fewer needed interparticle connections along the vertical path.

As for ionic resistivity ($N_m$ in Figure 3-8h), a more significant difference is observed, with the vertical orientation producing a less tortuous path as expected. The lower AM surface area (i.e. the exposed surface area to CBD and pore phases) for the horizontal case implies high connectivity between active particles, which can make the tortuosity higher. The random-orientation electrode is the combination of the horizontal and vertical cases and therefore its ionic transport behavior falls between the limiting cases. The relative effect of initial particle orientation is less pronounced after calendering for both ionic and electronic pathways. In other words, calendering tends to reduce the effect of initial differences.

It would be generally expected that ionic and electronic transport would be inversely correlated, meaning that any change that would increase one would decrease the other and this is observed here. However, in this instance, ionic resistances are more sensitive to changes in orientation than are electronic resistances.

The slightly higher Young’s modulus of the vertically-oriented dried electrode is expected from standard mechanical analysis in the field of composites (typically in the context of fiber composites), meaning that maximum resistance to deformation is found in the direction of the longest particle length [140].
Figure 3-8. Simulated cross sections for (a) horizontal, (b) random, and (c) vertical orientations of disk-shaped AM. Remainder of properties (d-i) are the same as those in Figure 4-5.
The model has the capability to predict the orientation evolution during drying and calendering steps. It is natural to attempt to validate the model results. To the best of the authors’ knowledge, the transport and mechanical properties for different active material orientations have not been studied for Li-ion electrodes, so there are few experimental results to validate the predictions made here. We have made 2D cross-sections of graphite electrodes in order to obtain some qualitative information on microstructures. Nevertheless, it is important to recognize that such images do not have adequate information content to perform a full structure comparison between the simulation and experiment.

Figure 3-9 gives representative SEM cross-sections of a graphite anode after coating, drying, and calendering, and qualitative differences are observed. Figure 3-9a shows the microstructure of the anode after coating, obtained by freeze-drying the wet sample. Many particles are horizontally aligned although some level of randomness is also observed in the structure. Such horizontal alignment could be due to the shear stress applied by the doctor blade during the coating process. This is in agreement with previous studies that observed the tendency of elongated particles to align to the flow streamlines [124, 130]. After drying (Figure 93-b), particles still align horizontally, though with increasing orientation randomness toward the top surface of the electrode. However, after calendering, more particles appear to align horizontally due to the vertical compression. To better tie these SEM images to the model results quantitatively, Figures 3-9b and 3-9c were segmented to get the porosity of the films. The porosity values of the dried and calendered structures are 0.42 and 0.30 respectively which is close to the porosity values of the horizontal case in Figure 3-8 (0.43 and 0.30 respectively). We also tried to relate the directional properties of the 2D cross-sectional images (Figures 3-8 and 3-9) to the frequency spectrum in the 2D Fourier domain [141]. However, we found the experimental images (Figure 3-9) did not
contain sufficient information to exceed noise levels to make quantitative conclusions. Thus, these experimental results can only qualitatively confirm the model predictions, which indicate that an initial horizontal orientation of particles can slightly change during different manufacturing steps. Therefore, if preferred orientations could be maintained, then modest improvements to electrode performance are possible.

Figure 3-9. SEM image of a graphite anode at 3 stages of manufacturing: (a) pre-dried, (b) dried, (c) calendered.
3.4.4 Active material stiffness

Figure 3-10 shows the physical and transport film properties for two disk-shaped AMs with different rigidities. The stiff case was given a Young’s modulus higher than typical for graphite and more characteristic of cathode materials. (Specifically, the higher modulus matches that for the HE5050 cathode in our previous study [98].)

After drying, the stiff particles do not agglomerate as much as for the soft case. This is shown by the higher film thickness, porosity, and exposed surface area of the AM in contact with CBD and pore phases. The stiff case leads to lower ionic resistance as lithium ions can travel through the more connected pores between the particles. The stiff case likewise reduces the electronic conductivity due to poorer contact between active particles. Finally, the higher Young’s modulus of the dried electrode is the result of stiffer active particles even though it is a less-dense structure.

Calendering does not diminish the property differences between the soft and stiff cases in general. However, calendering affects the relative ionic transport in the soft case more dramatically: calendering increases the MacMullin number by factors of 2.1 and 1.2 for soft and stiff cases respectively.
Figure 3-10. Simulated cross sections for (a) soft and (b) stiff AM. Remainder of properties (c-h) are the same as those in Figure 4-5.
3.5 Conclusion

The prediction capability of the model is used here to investigate the effect of different AM properties (i.e. size, shape, orientation, and stiffness) on electrode thickness, porosity, conductivities, and Young’s modulus. The effect of AM properties on microstructure features of anode-like materials may be summarized as:

(1) The AM size distribution had little effect on MacMullin number of dried electrodes, though there was a slight noted reduction in ionic resistance for the large-particle case after calendering.

(2) Although one would expect smaller particles to have more surface area, in practice the greater degree of aggregation means that exposed or electrochemically active area is not necessarily higher when compared to larger particles.

(3) As expected, smaller AMs create better contacts among active particles that can boost electronic conductivity compared to larger particles. In the case of variable AM sizes, smaller particles will fit into gaps between larger particles giving the mixed-size case higher electronic conductivity than for the large-particle case.

(4) The shape of the AM affects the packing density of the electrode that subsequently alters the transport properties of the electrode. Spheres tend to provide more electronic pathways before calendering due to higher packing density.

(5) The orientation of an irregular disk-shaped AM appears to have little effect on electronic transport and a more significant effect on ionic transport. Note that these results are based on initial orientations prior to the drying process, during which orientation differences start to diminish. Calendering clearly rotates disk-shaped particles to a more flat
orientation, but this has little effect on the property trends already evident at the end of drying.

(6) The AM stiffness, when changed independently from other particle characteristics, had a significant effect on all the determined electrode properties. This suggests that this is a particle property worthy of further investigation.

These results can guide material selection and electrode design by improving our understanding of fundamental interactions at the particle level and their relationship to electrode properties of interest. For example, the MPSP model results suggest that small soft spherical particles favor electronic pathways. Whereas, the model results suggest using large stiff rods that are oriented vertically when the goal is to maximize ionic conductivity. The model also suggests that gradient-type electrodes could take advantage of the differences in electronic and ionic transport with changes to active material morphology.

Finally, it is worth mentioning that fabricating a perfectly homogenous microstructure is both challenging and expensive. It involves meticulous monitoring of the particle size, shape, orientation, and stiffness plus the subsequent microstructure properties during different manufacturing processes. The results of this work provide some information for designing new electrodes with purposeful through-plane heterogeneity. In future work, the MPSP model can be used to assist the design of multi-layered electrodes, i.e., having a gradient in porosity achieved using a dual slot die process.
4 ELECTRODE MICROSTRUCTURE EVOLUTION DURING DRYING

4.1 Introduction

Li-ion electrode fabrication involves multiple steps: mixing, coating, drying, and calendering [53, 61, 142, 143]. There have been studies on these steps but not all conclusions are consistent. For instance, previous studies have observed the migration of binder inside the electrode during the drying process and proposed different explanations [52, 53, 144, 145]. Some of these studies show different and sometimes contradicting effects of the drying conditions on electrode performance [52, 53, 85, 146, 147]. For example, one study proposed that there is a receding consolidation layer (i.e. a crust) starting from the top surface [85]. Later on, this hypothesis was refuted by the same group when they showed that film shrinkage happens homogenously during drying [147].

Note that the redistribution problem of binder is a separate issue from the overall electrode formulation, meaning that even when there are adequate overall amounts of active, carbon, or binder in an electrode, they may not be optimally distributed. For example, scarcity of conductive carbon black and binder near the current collector can contribute to detachment of the electrode film from the substrate, affecting the contact resistance. This will in turn affect the electrochemical reaction on the active material surface and raise the cell overpotential.

Another issue is with the standard commercial quality-control methods that are done after calendering. They might not detect problems that arise at earlier stages. For instance, optical defect
detection is not sufficient to address all the heterogeneities that can develop during manufacturing. Furthermore, there is no standard method for binder migration detection.

Binder migration refers to the accumulation of binder on the top surface of the electrode which is associated with reduced cell performance in one case [85] but seems to not be problematic in another study [148]. Even though this phenomenon has received some attention in the battery academic community, the drying conditions where binder migration become an issue for electrode transport properties are still unclear. Plus, most studies have been conducted for anodes. Therefore, this work addresses the binder migration issue for two representative cases, an NMC532 cathode and a graphite anode, and focuses on determining the drying conditions where binder migration becomes significant. Furthermore, the extent to which calendering worsens or mitigates the effect of drying-induced defects is examined. This is done by tracking the atomic distribution and charge transport non-uniformities that initiate during drying and remain even after calendering [5]. Studying the electrode microstructure while it is drying is challenging due to three main reasons: (1) The battery slurry is opaque, consisting of high solid contents. (2) The drying process involves a multi-phase system with both liquid, solid, and pores that can limit the detection of microstructure evolution because in situ scanning electron microscopy (SEM) cannot be used. (3) The slurry is coated as a thin layer that is usually dried at high rates, making tracking the phase transition even harder.

To address these challenges, we developed a lab-scale freeze-drying technique that can preserve the microstructure before the electrode film is conventionally dried. The freeze-dried and regularly dried microstructures are then compared using SEM. Multiple drying rates are studied by changing the drying temperature. This way, the effects of convection, diffusion, or possible
sedimentation can be distinguished, as the first two are amplified at a high drying rate while the last effect is more pronounced at a lower drying rate because particles have more time to settle. Such effects are quantified by tracking microstructure and charge transport properties. Electrochemical performance properties of the electrodes have not been tested yet but could be part of future work.

**Electrode microstructure properties:** Based on our previous modeling study [5], we expect the bottom and top surface of the electrode to respond to the drying process differently than does the interior region. Therefore, the in- and through-plane directions elemental composition heterogeneity are analyzed based on SEM cross-sectional images and energy-dispersive X-ray spectroscopy (EDS). This analysis can help determine the non-uniform particle distributions across and through the film thickness. To ensure the reliability of the conclusions, three different electrode cross-sections (250×175 μm² area) from two separate batches of NMC cathode and graphite anode are studied for the microstructure properties.

**Electrode transport properties:** Another way of quantifying the effect of drying rate on the electrode microstructure is to measure the ability to transport charge. The local and overall differences in electronic and ionic transport are a reflection of the microstructure differences among the electrodes dried at different rates. Electronic and ionic maps provide local charge transfer data over a 2.4×2.4 cm² electrode area. A flexible micro-contact probe is used to measure the electronic conductivity [149]. The ionic resistivity is expressed as a MacMullin number based on localized blocking-electrolyte measurements [150]. These maps are intended to provide an areal presentation of the transport properties variability. The average electronic conductivity and ionic resistivity can help identify the optimal drying rate (temperature) that results in a lower transport
resistivity. We also compare results between dried and calendered structures to assess the persistence of effects due to the drying rate.

The remainder of this chapter consists of a description of the drying and calendering processes (Section 2), the experimental design and the simulation setup (Section 3), and a discussion of results for the NMC532 cathode and graphite anode dried at different rates (Section 4).

4.2 Drying process

This section reviews what is known about microstructure evolution during the drying process. We are particularly interested in how solvent evaporation leads to a particular microstructure and the resulting electrode defects.

4.2.1 Electrode drying process

Battery slurries are suspensions consisting of a high amount of solid material (active material and conductive carbon) that are dispersed in a liquid containing a polymeric binder. The solid particles are subject to random Brownian motion in the liquid medium. Such random movements and other existing forces (e.g., gravitational) affect the microstructure properties during different fabrication steps. Such effects are reflected in slurry rheology during mixing and coating processes as well as the phase distribution in the subsequent dried and calendered porous structures [151]. The focus of this work is on drying and calendering steps.

Evaporation (convection), diffusion, and sedimentation are happening simultaneously during electrode drying [152]. The final location of the electrode components and the subsequent electrode features are determined by these phenomena. For example, the convective and capillary forces cause the binder to migrate toward the top surface whereas some of the binder particles can
still diffuse back toward the substrate (binder homogenization) through the presently connected solvent reservoirs [85, 147]. Sedimentation due to gravitational force and density differences mostly affects the active material distribution, as the denser phase compared to CBD and solvent. However, sedimentation is not significant except at high temperatures given the high viscosity of the Li-ion electrode slurry [153].

Among the different solid components of the battery slurry, the carbon black and binder are more subject to capillary-pressure-driven migration (redistribution). This can be due to the small particle size of 50nm and ~15nm (single chain) for carbon black and binder respectively [154] where gravitational forces have little effect on them.

The drying mechanism is illustrated in Figure 4-1. It is frequently divided into constant-rate and falling-rate regimes. In the battery community, some researchers instead divide the process into consolidation and pore-emptying regimes [47, 52, 53, 144, 147, 153, 155-157]. These two ways of dividing the drying process are not exactly the same in an electrode film.

During the consolidation regime, the solvent evaporates from the top surface at a constant rate and the electrode thickness starts to decrease as the solid particles move closer together.

At the end of film shrinkage (Figure 4-1b), when the hard active particles get in contact to establish a skeleton, a capillary network is developed throughout the electrode film. Some pores start to empty as a result of evaporation and the remaining pores will deliver more solvent to the emptying ones because of capillary action (Figure 4-1c). Assuming the solvent tends to wet the surface of the solid particles, capillary forces cause the solvent to flow from large (nearly empty) to smaller (fully or partially saturated) pores. Note that solvent evaporation still takes place at a constant rate from any saturated liquid reservoirs (Figure 4-1d).
At this point, the solvent distribution is not uniform across the thickness of the film meaning that larger pores empty first regardless of their location [53]. Therefore, the electrode drying is not just the liquid level dropping.

Figure 4-1. Illustration of the electrode film drying mechanism: (a) through (b) is consolidation step, (c) through (d) is pore-emptying, (e) dried electrode, and (f) the drying curve.
Near the end of drying, any remaining isolated solvent cluster has to overcome an additional transport resistance through the gas phase of the empty pores. This results in a decreased mass transfer and a falling-rate regime [158, 159]. As shown in Figure 4-1f, the majority of the drying process happens in the constant-rate regime where small pores remain saturated during most of the electrode drying [53].

A simulation of this capillary-driven drying mechanism is described in Chapter 2 and called the network-favored model of the drying process [5].

4.2.2 Electrode defects from the drying process

Studying thin-electrode microstructure is challenging due to the phase transition of a multi-component system that is subject to significant changes during a short amount of time. Three types of deleterious physical changes have been observed for Li-ion electrodes during drying: particle redistribution, electrode delamination, and cracking. These changes can lower cell capacity [53, 85, 144, 147, 160].

Material redistribution (migration): There are multiple sources of particle redistribution. As previously mentioned, the pressure gradient among pores drives the capillary movement of solvent. The same solvent movement can drag carbon black and binder to the top surface. Another instance is when the moving liquid-vapor interface causes the binder that is dissolved in the solvent during the mixing process to be left behind as part of the solid phase. The third redistribution example is when CBD particles as the more mobile phase fill the extra gaps between the inefficiently packed large and stiff active material particles at the current collector surface [5]. This redistribution results in a higher CBD content near the electrode-substrate interface after drying.
It is worth mentioning that we are not referring to other types of non-uniformities formed prior to the drying step. For example, a not-well-mixed slurry has non-uniform distribution in different directions.

This particle redistribution is usually tracked using EDS to quantify the fluorine content as the most distinguishable element in the carbon-binder domain (CBD) [157].

Binder type and solvent type affect the particle redistribution during drying. For instance, PVDF binder which is widely used in battery electrodes has less affinity to the active material than does carboxymethyl cellulose (CMC) or polyvinylpyrrolidone. Therefore, PVDF has higher a chance of redistribution during drying [161, 162]. The solvent type can also affect particle redistribution. It has been shown that organic-based NMP slurries are more subject to non-uniform binder distribution compared to water-based electrodes. This is due to the higher boiling point of organic-based solvent that can prolong the constant-drying regime which allows the migration of binder for a longer time [163].

Therefore, a more detailed investigation into this particle redistribution is necessary to learn more about the drying mechanism of Li-ion electrodes and how they affect microstructure properties or defects.

*Electrode delamination:* The separation of electrode film from the substrate is called delamination. Any shearing forces that would overcome adhesion will cause delamination. The electrode film shrinks in all directions during drying and a cohesive bond starts to form between electrode components due to the binder. The electrode microstructure can shrink freely in the through-plane direction but the current collector resists the in-plane shrinkage. This unrelieved stress in the in-plane direction can cause delamination when it is greater than the adhesion to the current collector. Thicker electrodes are more prone to delamination due to the higher probability
of cohesion overcoming adhesion given there is more electrode (raising cohesion) material within the same area (same adhesion).

Binder depletion at the film/substrate interface as a result of binder redistribution during drying can be also responsible for electrode delamination. Previous studies on graphite anodes show that the adhesive forces are lower at higher drying temperatures (56°C versus 31°C) [164].

Electrode cracking: Similar to electrode delamination, forming cracks on the electrode is the result of residual stresses inside the film after drying. Previous studies showed that electrode cracking is more probable for thicker electrodes and at higher drying rates [144]. Such particle disconnection can decrease electronic transport across the crack which is especially detrimental when they are in the in-plane direction. Note that through-plane cracking is not necessarily undesirable because it opens up ionic transport. This can be compared to traditional pores inside the electrodes which can be considered as small cracks that facilitate ion movement.

4.2.3 Defect mitigation methods

As mentioned previously, these defects directly affect cell-level performance. Therefore, many of them need to be addressed for designing the next-generation Li-ion electrodes with a superior lifetime. This can be achieved by: (1) decreasing the drying rate which can reduce particle migration, (2) reducing the solvent surface tension which leads to less capillary forces that drive binder migration [58], (3) increasing the elastic modulus of the solid component which can lead to higher mechanical stability, and (4) adding an inactive additive like a second polymeric binder (increasing the dry bonds), or a second solvent like isopropyl alcohol (reducing the stress inside the electrode) [156, 165].
Changing the electrode components or adding non-active material is not necessarily desirable especially if it leads to lower electrode energy density or requires synthesizing a new electrode material. However, particle redistribution is something that can be controlled by modifying the drying process so that a desirable particle arrangement is achieved. Controlling the drying rate is the most practical approach that can be applied to the drying process at any scale. Previous studies suggest a lower yet unidentified drying rate to minimize the particle redistribution even though a higher drying rate is more economical from the production point of view [52, 53]. For example, a multi-step drying scheme can be devised to minimize binder migration. A three-stage drying protocol can minimize the capillary forces that lead to binder migration; an initial high drying rate followed by a low to moderate rate in the middle (when the first pore starts to empty) and then a high rate near the end of drying can make sure that the majority of binder migration happens during the low to moderate rate step [147].

In conclusion, the drying process can alter electrode microstructure and its physical and performance properties. But it is not the final fabrication step. The next step, calendering, can magnify or eliminate the drying effects.

4.3 Calendering process

Calendering (electrode compression between two metal rollers) is known to improve the quality of the dried film by smoothing out the thickness variations [166]. However, the work discussed in Chapter 2 shows that is not always the case. The variability in electronic conductivity and ionic resistivity increase after calendering due to an additional CBD particle redistribution [5]. Another study showed that cracks formed during drying are not fully diminished after calendering [58].
Despite the fact that most batteries are composed of calendered electrodes, few studies have been conducted to investigate if calendering can mitigate the binder migration issue. Therefore, in this work, we investigate the effect of calendering as well. The in-house fabricated NMC532 cathodes and graphite anodes are dried at different temperatures. The effect of drying rate is investigated by measuring the transport properties. Then the electrode is calendered and the transport property measurements are repeated.

4.4 Experimental design

4.4.1 Electrode fabrication

The electrodes used in this work are fabricated as follows. Table 4-1 summarizes the dry electrode formulations. The LCO electrode is used for freeze-drying experiments, and graphite and NMC electrodes for further drying tests. First the active material and carbon black were ground by a mortar and pestle for 20 minutes to break up aggregates and disperse carbon black in the active material. NMP solvent and PVDF binder were mixed separately for 30 minutes to activate the binder and to have a uniformly dispersed mixture. All the components were then wet-mixed using a high-speed immersion blender for 20 minutes over an ice bath to prevent the heating of the slurry and the accompanying evaporation of NMP. The electrodes were coated on a metal foil using a doctor blade.

Graphite and NMC electrode drying took place in a convective oven for 10 minutes at different film temperatures in the range 80-232°C as discussed below. One set of electrodes was dried at room temperature for 12 hours. Electrode electronic and ionic transport properties were then tested. Then the films were calendered at room temperature between two metal rollers. The thickness loss during calendering was 14% for all the dried electrodes.
Table 4-1. Electrode formulation.

<table>
<thead>
<tr>
<th>Active name</th>
<th>Active (wt%)</th>
<th>Carbon black (wt%)</th>
<th>Binder (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCO</td>
<td>90</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>NMC</td>
<td>90</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Graphite</td>
<td>92</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

4.4.2 Freeze-drying

To validate the drying step, one can monitor the weight of the sample during an experiment, but that does not provide information on the microstructure. Therefore, a freeze-drying technique was used to capture the wet coating structure, complementary to cross-sections captured after regular drying.

Freeze drying is a technique widely used to preserve the structure of solids within a wet sample. In this method, the coated slurry is cooled below the solvent triple point, which is -24.0°C and 0.54 Pa for NMP [167], and the temperature is controlled carefully to ensure that sublimation occurs rather than melting. During the freeze-drying process, the vapor pressure of NMP in the sample container is much lower than the vapor pressure of the sample and this will force the solvent molecules out of the sample. The rate of sublimation depends on this difference in vapor pressures as well as diffusivity and convection.

Figure 4-2 shows the freeze-drying setup. The compressed air is initially dehydrated by silica gel beads, cooled down by liquid nitrogen with an additional dehydration step to guarantee that there is no ice interfering with the sublimation of NMP. All the solvent particles are eliminated within 6 hours by carefully monitoring the sample temperature (27.5 ± 3 °C). The SEM images are taken to study the final structures.
4.4.3 Electrode cross-section imaging and analysis

*SEM/BIB:* The electrode films were milled using a broad ion beam (IB-19530CP JEOL cross-section polisher) for 2 h at an ion beam voltage of 5 kV. ThermoScientific Apreo C scanning electron microscope (SEM) was used to study the uncalendered electrode microstructure differences when dried at different temperatures.

![Figure 4-3. The milled cross-section of the cathode dried at 232°C (left) and the segmented image (right). Yellow represents the active material, red shows CBD, and pores are colored light blue.](image)

*Image segmentation.* Segmentation is assigning distinct material phases to different regions of the cross-section image. Segmented images can be used to obtain volume fractions of the different phases. In this instance, SEM images were processed using a multi-band thresholding
method [168] accompanied by manual corrections to distinguish among different phases (pore, carbon-binder, or active material), with the end result illustrated in Figure 4-3.

**EDS:** Energy-dispersive X-ray spectroscopy was performed (ThermoScientific Verios G4 UC SEM) to get the elemental distributions of milled cross-sections of the uncalendered cathode and anode. Two types of analysis were done to quantify the fluorine content of the binder as its most distinguishable element. First, a four-layer quantification analysis in which cross-sections were divided vertically into four similarly sized rectangles. Fluorine is difficult to detect given the low atomic mass and the small amount of binder used in these electrodes. Therefore, we need a big enough area to get a good signal, hence dividing the cross sections into four rectangles. The fluorine distribution was determined based on the elemental normalized to the total fluorine weight fractions across the film cross section. The acceleration voltage was 15 V and the total x-ray counts were over two million in each spectrum to get a good signal-to-noise ratio. The second type of analysis was an elemental map which shows an example of a semi-quantitative binder distribution based on a superimposed fluorine distribution across the uncalendered film. Each of these analyses was repeated three times but only one is shown.

### 4.4.4 Electrode testing

**Electronic conductivity.** Electronic conductivity measurements were conducted using a flexible surface probe over a 25×25 grid of points (1 mm spacing) on the electrodes. An input voltage of 2.5 V was used for cathodes and 1.0 V for the anode. Lower voltage for the anode is due to the higher conductivity of the graphite active material. A model was used to invert the experimental measurements to electronic conductivity and contact resistance of the films [149].
**Ionic conductivity.** The ionic conductivity of the films was determined using a localized blocking-electrolyte measurement [150]. Each electrode was first soaked in an electrolyte (25.8 mM tetrabutylammonium hexafluorophosphate (TBAPF6) in propylene carbonate). After sitting for 24 hours to allow wetting, we used an aperture probe to conduct localized ionic measurement on each electrode with a 25×25 grid of points (1 mm spacing). The typical contact pressure between probe and sample is 73 kPa. While the sample was in contact with the probe, an EIS spectrum was collected with frequencies varying from 4 kHz to 0.1 Hz and a perturbation of 50 mV. After the measurement, impedance data were fitted to MacMullin numbers using a 2D cylindrical transmission line model [150].

### 4.5 Results and discussion

#### 4.5.1 Freeze-drying

The comparison between the freeze-drying and regularly-dried electrodes is shown in Figure 4-4. There are some uncertainties and difficulties in analyzing these results due to the heterogeneous electrode film and the non-uniform particle shape that results in different particle packings and mass loadings.
Figure 4-4. (a) The SEM image of a freeze-dried LCO cathode, (b) the segmented freeze-dried, (c) the SEM image of a regularly-dried electrode, and (d) the segmented image of the regularly dried. Yellow shows the active material, red represents CBD, and light blue is the indication of pores.

One interesting observation is that the freeze-dried image shows the CBD as a distinguishable phase that probably forms before drying (most likely during mixing). The macropores in the freeze-dried electrode show the solvent reservoirs that are sublimated. Furthermore, the CBD phase in the freeze-dried image (Figure 4-4a) is more dense and less porous compared to the regularly-dried electrode (6% and 17% respectively).
Similar to model results in Chapter 2, these results suggest that drying is more likely to affect the CBD phase rather than the active materials. In the next part, we study the effect of drying temperature on the electrode microstructure and transport properties.

4.5.2 Anode microstructure changes with drying temperature

Figure 4-5 shows how the dried anode microstructure changes as the drying temperature increases. At 24°C, the CBD phase is more like a non-porous cluster on the active material. As the drying temperature increases, CBD starts to become more porous and the binder starts to form visible bonds between the active materials (Figure 4-5d).

Figure 4-5. SEM images of the dried graphite anode at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.
Table 4-2 reports the porosity of the dried films (determined from the electrode film thickness and the segmented images). The results show that the overall electrode porosity is around 45 to 50% regardless of the drying temperature which can be due to the soft graphite that is crushed by micrometer during thickness measurement. On the other hand, the segmented images of the anode electrodes have higher porosity at higher temperatures but there is still no linear correlation between the drying temperature and porosity. This can be due to the irregular shape of the graphite active material that can align in different directions during the consolidation phase. The following discussion on MacMullin numbers (Section 4.5.9) can provide more information about these structures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Overall anode porosity</th>
<th>Segmented anode porosity</th>
<th>Overall cathode porosity</th>
<th>Segmented cathode porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>48.4</td>
<td>21.0</td>
<td>53.9</td>
<td>51.9</td>
</tr>
<tr>
<td>80</td>
<td>49.1</td>
<td>28.8</td>
<td>41.5</td>
<td>37.8</td>
</tr>
<tr>
<td>150</td>
<td>44.8</td>
<td>53.4</td>
<td>39.5</td>
<td>21.1</td>
</tr>
<tr>
<td>232</td>
<td>48.4</td>
<td>34.4</td>
<td>39.8</td>
<td>17.5</td>
</tr>
</tbody>
</table>

4.5.3 Cathode microstructure changes with drying temperature

Figure 4-6 shows how the microstructure changes for NMC cathode as the drying temperature increases. The CBD phase is more distinguishable for cathodes compared to anodes.
At 24°C, CBD is less porous and more macropores exist in the film. As the temperature increases, the active materials come closer together and the CBD phase fills the space between the active material. This trend is also shown in both overall and segmented porosity of the cathode films as shown in Table 4-2. As the drying temperature increases from 24°C to 80°C, overall and segmented porosities decrease 12.4 and 14.1% respectively. Beyond 80°C, the overall porosity doesn’t change drastically but the segmented porosity continues to decrease.

Figure 4-6. SEM images of the dried NMC cathodes at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.
4.5.4 Binder distribution in through- and in-plane directions

In this section, a more detailed analysis of binder distribution is presented to find out under what conditions the MPSP model predictions are observed in the experiments. In Chapter 2, we discussed that the CBD content is pretty uniform across the film thickness with a slight peak at the current collector side which was contradictory to previous studies by other groups [52, 53, 169]. As a side note, the temperature range for binder migration is determined for both cathodes and anodes. Furthermore, sufficient data is provided to account for electrode heterogeneity in both through- and in-plane directions.

Binder distribution in graphite anode. Figure 4-7 shows the quantitative analysis of the fluorine element content at four different regions (region 1 is adjacent to the separator and region four is next to the current collector as shown in Figure 4-7e). The results show that binder distribution is not uniform in both through-plane (shown as the bar charts) and in-plane (shown as the error bars on the bar charts) directions.
Figure 4-7a shows higher fluorine content at the top surface of the electrode even at 24°C which suggests that the binder that was dissolved in the solvent is left behind at the top surface. The expected binder migration appears at 150°C with lower fluorine content near the current collector (Figure 4-7c) although it is not uniform at other cross-sections as well (as indicated by
the large error bar in region 4). At the higher temperature of 232°C, even a more fluorine fraction is observed in region 2.

![Figure 4-8. Fluorine elemental map for anodes dried at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.](image)

The fluorine elemental maps are shown in Figure 4-8, revealing interesting information about the relationship between these experiments and our previous simulations in Chapter 2. These results suggest that the MPSP model results correspond to a drying temperature range of 80-150°C where more fluorine (the representative element of CBD in our simulation) accumulates on the bottom surface of the electrode and fills the space created by the inefficient packing of active material particles.

The high drying temperature required for binder migration suggests why there is less attention to binder migration in the battery industry. This is due to the conventional lower drying temperature range (60-80°C) used on a large scale.
Binder distribution in NMC cathode. Figure 4-9 shows the quantitative EDS results for the NMC cathode. Similar to anode results, the fluorine non-uniformity exists in both through- and in-plane directions. The binder non-uniformity starts to emerge at temperatures higher than 150°C although it is not the case at all cross-sections (large error bar in Figure 4-9c).

Therefore, the previous modeling results also correspond to the drying temperature of 80°C where there is slightly more binder content at the current collector and no binder migration is detected.

There could be some fluorine detection problems when there is variation in electrode porosity. Porosity difference results in fluorine weight percent differences among different samples (dried at different temperatures) even though all of them were obtained from the same batch with similar compositions and pre-dried fabrication steps. This can be due to EDS detection limits that were previously ignored. EDS quantification theory states that the sample needs to be flat and homogenous at the atomic level. None of which are entirely true for battery electrodes. The milled active material surface is flat but that is not the case for porous CBD. Therefore, the x-ray detection will skew if there is a porosity difference among the samples. Because the x-rays need to go through more material versus when they hit the surface. Furthermore, fluorine generates high-energy X-rays. This high energy can be absorbed by other elements like manganese or oxygen in the active material If fluorine is trapped inside the pores. The absorbed energy can excite the inner shell electron and generate new X-rays. The detector will recognize these new X-rays as the cathode active material, not fluorine which would eventually change the apparent composition.
Figure 4-9. Normalized fluorine fraction at four regions (1 is at the top and 4 at the bottom) of cathodes at different drying temperatures of (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.

4.5.5 Anode electronic conductivity

The electronic conductivity of an anode is an indication of its ability to transport electrons through a combination of conductive carbon and graphite active material. Figure 4-10 shows the electronic conductivity distributions of anodes dried at different temperatures. At 24°C, most of the electrode shows an average electronic conductivity of around 3000 mS/cm. When we increase the temperature to 80°C, the average electronic conductivity increases to more than 3500 mS/cm but it is less uniform. At temperatures higher than 150°C, the electronic conductivity starts to decrease. This can be due to the higher porosity of anodes dried at high temperature (based on segmented anode porosity in Table 4-2), the visible in-plane cracks (shown in Figure 4-8c), or the
temperature-dependent conformational changes of PVDF binder. Lower drying temperatures are reported to favor PVDF conformation with the highest electronic conductivity [170].

Figure 4-10. Electronic conductivity maps of uncalendered anodes dried at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.
Figure 4-11. Electronic conductivity maps of calendered anodes dried at (a) 24°C, (b) 80°C, (c) 150°C, (d) 232°C, and (e) comparison between the average electronic conductivity of anodes before and after calendering.

Calendering increases the electronic conductivity of all electrodes by making a more compact microstructure (Figure 4-11). Such increase is more noticeable for the lowest and highest
drying temperatures of 24°C and 232°C. This results in a similar electronic conductivity of around 3800 mS/cm for anodes dried at 24°C and 80°C versus 2000 mS/cm for the ones dried at 150°C and 232°C. These results suggest that calendering can diminish the effect of drying rate to some extent but lower drying temperatures still result in higher electronic conductivity even after calendering.

Similar to the results presented in Chapter 2, the amount of variability (demonstrated by the size of the error bars in Figure 4-11e) increases for the anode after calendering due to particle redistribution.

### 4.5.6 Cathode electronic conductivity

Similar to the anode results, the uncalendered cathode also shows a maximum electronic conductivity at 80°C drying temperature (Figure 4-12b). However, the microstructure is less uniform compared to other drying temperatures. This can be due to the intermediate microstructure with a mixture of high- and low-temperature characteristics. At low temperatures, there are some gaps between the active material and CBD phase (Figure 4-6b) plus the binder is not fully activated [81]. At higher temperatures, the microstructure is less porous which promotes higher electronic conductivity.

It is worth noting that in the actual cell, the maximum electronic conductivity is not the only important factor. It is rather a balance between the electronic and ionic transport properties of a given electrode and the match between the cathode and anode properties that can partially determine the cell kinetics and cycle life.
Figure 4.12. Electronic conductivity maps of uncalendered cathodes dried at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.

The trend for calendered cathodes is similar to that for the dried ones, namely the 80°C drying temperature results in the highest electronic conductivity (Figure 4-13). The electronic conductivity of the cathode is more uniform after calendering. This result is different than what was presented in Chapter 2. This can be due to the milder calendering process used for these electrodes compared to the calendered cathodes discussed in Chapter 2. Those electrodes were calendered to a higher degree to reach the desired 35% porosity. Their thickness change was about 20% of their initial uncalendered thickness compared to 14% for the electrodes in this chapter.
These results suggest that increased variability in the cathode after calendering can be a function of calendering degree.

Figure 4-13. Electronic conductivity maps of calendered cathodes dried at (a) 24°C, (b) 80°C, (c) 150°C, (d) 232°C, and (e) comparison between the average electronic conductivity of cathodes before and after calendering.
4.5.7 Anode contact resistance

The contact resistance of an electrode provides more information about the electrode-substrate interface; higher contact resistance can mean that the electrons face a higher barrier at the interface, consuming energy during cell charge and discharge. High contact resistance can be due to the large pores, cracks, or delaminations formed at the interface instead of the electronically conductive active material or carbon black. Figure 4-14 shows the contact resistant results of the uncalendered anodes dried at different temperatures. The contact resistance increases with drying temperature. The uncalendered anode dried at 150°C shows both higher contact resistance and higher spatial variability. This can be due to the non-uniform distribution of binder in both the through- and in-plane directions (Figure 4-7c).

Figure 4-14. Contact resistance maps of uncalendered anodes dried at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.
Figure 4-15. Contact resistance maps of calendered anodes dried at (a) 24°C, (b) 80°C, (c) 150°C, (d) 232°C, and (e) comparison between the average contact resistance of anodes before and after calendering.

The lower contact resistance of electrodes dried at low temperatures can be due to the more uniform binder distribution (Figure 4-7) and lower segmented porosity (Table 4-2).
Figure 4-15 shows the contact resistance of the calendered anodes. After calendering, the contact resistance decreases for all anodes as a result of better compaction near the current collector and the subsequent particle redistribution as discussed in Chapter 2.

### 4.5.8 Cathode contact resistance

The cathode contact resistance and its variability increase with the drying temperature (Figure 4-16). This appears to be due to the binder distribution near the current collector (Figure 4-9). At lower temperatures of 24°C and 80°C, enough binder exists at the film-substrate interface creating sufficient connections. However, at high temperatures, the number of these bond starts to decrease due to binder migration toward the top surface.

![Contact Resistance Maps](image)

Figure 4-16. Contact resistance maps of uncalendered cathodes dried at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.
Figure 4-17. Contact resistance maps of calendered cathodes dried at (a) 24°C, (b) 80°C, (c) 150°C, (d) 232°C, and (e) comparison between the average contact resistance of cathodes before and after calendering.

Calendering does not qualitatively change the previously observed trend of drying temperature for the NMC cathode (Figure 4-17). It decreases the contact resistance and its variability for all
electrodes. This can be due to calendering compression and the proposed binder redistribution discussed in Chapter 2, namely the multi-phase packing theory.

4.5.9 Anode ionic resistance

Ionic resistance which is expressed in terms of MacMullin number shows how tortuous is the ionic path inside the electrode film. Higher MacMullin numbers reflect higher tortuosity (Equation 2-1). Figure 4-18 shows that with increasing the drying temperature, the MacMullin numbers increase throughout the electrode area. The binder migration during the drying process can explain this observation. This is due to the fact that local ionic measurements are more sensitive to the electrode tortuosity near the top surface [145]. The presence of more binder and conductive carbon on the top surface can lengthen the ionic pathways.

![Figure 4-18. Ionic resistance maps of uncalendered anodes dried at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.](image)
As expected, calendering will increase the MacMullin number as a result of lower film porosity and therefore fewer connected pores (Figure 4-19). The error bars in Figure 4-19e are
confirming our previous observation that the anode is more prone to heterogeneity due to its shape and orientation variability as discussed in Chapters 2 and 3.

### 4.5.10 Cathode ionic resistance

Figure 4-20 shows the contour maps of MacMullin numbers for cathodes dried at different temperatures. Similar to what is observed for the anode, the MacMullin number increases with temperature due to binder and carbon migration toward the top surface and the sensitivity of the measurement method to surface features. The nanoporosity of the CBD near the top surface can limit ion transports compared to Macropores. Another reason for the higher ionic resistance of cathodes at higher temperatures is the lower film porosity (shown in the cathode segmented porosity column in Table 4-2).

![Ionic resistance maps of uncalendered cathodes dried at different temperatures](image)

Figure 4-20. Ionic resistance maps of uncalendered cathodes dried at (a) 24°C, (b) 80°C, (c) 150°C, and (d) 232°C.
Figure 4-21. Ionic resistance maps of calendared cathodes dried at (a) 24°C, (b) 80°C, (c) 150°C, (d) 232°C, and (e) comparison between the average ionic resistance of cathodes before and after calendering.

After calendering, both the average and local MacMullin numbers increase due to compression and decreased porosity (Figure 4-21). The ionic maps for cathode preserve some traits
of MacMullin distribution after calendering due to cathode higher mechanical resistance (rigidity) toward compression, as discussed in Section 2.6.5 concerning Young’s modulus.

4.6 Conclusion

The drying process has a crucial effect on the Li-ion electrode microstructure and yet little is known about this fabrication step. This chapter provides an experimental study of the drying process for both a graphite anode and NMC cathode.

The experiments confirm the accuracy of the novel MPSP model predictions about binder redistribution near the current collector at conventional drying temperatures.

The EDS results show that these two electrodes respond differently toward drying conditions. Binder migration starts to appear at temperatures between 80°C and 150°C for the anode. Whereas the NMC cathode has a higher tolerance toward binder redistribution; it starts to get noticeable at temperatures between 150°C and 232°C.

Both cathode and anode show the highest electronic conductivity for the drying temperature of 80°C. This appears to be the result of more uniform binder distribution and higher electronic conductivity of a specific conformation of the PVDF binder.

Calendering has a diverging effect on anode electronic conductivity depending on the drying temperature. However, the trend of electronic conductivity with drying rate remains the same for cathodes after calendering. Regardless of the electrode type, the drying temperature of 80°C still results in the highest electronic conductivity.

The contact resistance of both graphite anode and NMC cathode increases at high temperatures as a result of fewer connections between the binder and current collector when the binder and the conductive carbon accumulate instead on the top surface.
The ionic resistivity trend of the electrodes dried at different temperatures suggests a possible limitation of the transmission line model used for blocking electrolyte measurement interpretation. Specifically, the model assumes a uniform MacMullin in vertical direction which means that it is producing an average MacMullin number weighted more toward the surface values. Carbon and binder redistribution can also cause higher ionic resistance at the upper surface where nanopores inside the carbon-binder-domain hinder ionic transport.
5 SUMMARY AND PERSPECTIVE

This chapter briefly summarizes the work that has been done in this dissertation and mentions some suggestions for future work.

5.1 Summary of the work

The next-generation batteries need further improvements to provide higher storage capacity. Higher energy storage requires full electrode volume utilization with minimal transport and kinetic limitations. This goal can be achieved by learning more about the cell starting point which is electrode fabrication. This work provides more information about the physics of drying and calendering fabrication steps and how electrode materials respond differently during fabrication processes.

A multi-phase smoothed particle (MPSP) model was parameterized and validated for four different electrodes by comparing experiment to simulation. The transport and mechanical properties of the electrodes were used as measures to quantify the microstructure features. The agreement between the experimental and simulated results inspired us to use it for further studies where few experimental work had been reported. An improved electrode design could be based on novel materials or it can use existing materials in a novel way. This work is intended to enable either option through greater understanding of the relationship between performance and fabrication processes combined with particle characteristics.
Finally, the unexpected result of the MPSP model for the dried electrode (where there is a slight increase in density for the CBD near the current collector) motivated us to do further study on the drying process in which we found the relationship between various material properties and the drying temperature for a typical anode and cathode.

5.2 Suggestions for future work

5.2.1 Designing a multi-layered electrode

The MPSP model can be used in different ways to help battery manufacturers design new electrodes with superior performance. One of those could be multi-layered electrodes. There is increased attention in the battery community to the idea that multi-layered electrodes can improve Li-ion battery performance although they are more difficult to manufacture. The idea of a multi-layered electrode is based on the Chapter 3 results where certain active material properties favor certain modes of charge transport. For example, the MPSP model results suggest choosing a small soft spherical active material for better electronic contact near the current collector. A preliminary simulation result for a dual-layered electrode is shown in Figure 5-1. This electrode consists of small disc-shaped active material particles (6µm) at the bottom and large ones (15µm) near the top surface.

The results show that although this electrode design delivers the desired higher electronic conductivity near the current collector, calendering seems to diminish the electronic conductivity difference between the layers and cause a noticeable difference in the MacMullin numbers in the reverse direction of what is desired which is lower MacMullin number on the top surface to facilitate the ion transport from the separator side. Using the MPSP model for further investigation
of this type of electrode design can suggest certain changes to fabrication to realize the possibility of superior performance.

Figure 5-1. A dual-layered anode after (a) coating, (b) drying, and (c) calendering. Yellow particles show active material, red represents the CBD, dark blue is the solvent, and the current collector is shown with grey particles. The electronic conductivity, MacMullin number, porosity, and active material surface area are reported in the boxes.

5.2.2 Mixing and coating simulations

Another possible extension of the current work is simulating the mixing and coating processes. There are some open questions relating to these processes just as there was for the drying process. For instance, insufficient electrode slurry mixing can cause particle agglomeration and non-uniform distribution, and there is no satisfactory model that describes this process for Li-ion battery slurries.

In the process of developing the MPSP model, it was intended that it could be used to simulate mixing and coating processes, and the required physics are naturally included. Indeed, the MPSP model was partially parameterized and validated using slurry viscosity experiments using a conventional electrode formulation. The biggest obstacle to statistically valid mixing and
coating simulations was the greatly increased size and time scales required compared to the drying and calendering simulations. Both types of simulations were attempted, and results were encouraging but a frequent problem was insufficient memory resources even on the BYU supercomputer platform for simulations of the correct size scale. We hope that additional computing resources can be deployed to solve the problem in the future. Nevertheless, we present below some preliminary experimental and simulation results to inspire possibilities for future work.

The amount of sufficient mixing can be quantified using the viscosity curve. The degree of mixing can change the viscosity of the electrode slurry at a specific shear rate which appears to be caused by changes in particle agglomeration. When a steady-state viscosity is reached, that can indicate a sufficiently mixed slurry [54]. For electrode slurries presented in this work, a steady-state is detected generally after 20 minutes of mixing. Usually, insufficient mixing is the biggest problem, though it may be possible to mix too much. One suggested drawback of excess mixing, at least for lab-scale operations, is shear-induced damage to the binder molecules.

![Figure 5-2](image.png)

Figure 5-2. Local variation in the composition of an LCO electrode mixed for 10 minutes: (a) SEM image, (b) segmented image.

Local composition variation results from insufficient mixing, and subsequently, the electrode characteristics will be non-uniform. As seen in physical experiments, insufficiently-
mixed slurry shrinks more dramatically during the drying step (thickness change of 55% vs. 30% for well-mixed slurry). The reason for this behavior could be the uneven distribution of binder that holds the structure differently during drying. Another consequence of this non-uniformity is the more frequent delamination of the unmixed film which has been observed experimentally.

Figure 5-2 shows the SEM image of an insufficiently mixed LCO slurry and its segmented image. The non-uniform distribution of the CBD clusters for an insufficiently mixed slurry can be simulated to predict the transport properties versus a well-mixed one.

![Figure 5-2](image)

Figure 5-3. The MPSP simulation of the mixing process by assuming a larger non-uniform CBD cluster distribution: (a) not well-mixed slurry, (b) CBD cluster distribution in a well-mixed electrode slurry, and (c) CBD cluster distribution in an unmixed electrode slurry.

Table 5-1 shows the simulated electronic conductivity and ionic resistivity of two slurries, one well-mixed and one not well-mixed, as shown in Figure 5-3. Smaller CBD clusters are beneficial for the electronic and ionic conductivity of the anode before calendering. Another advantage of having smaller CBD cluster is the lower ionic resistivity as the bigger CBD clusters
can block the pores. Therefore, MPSP model suggests sufficient mixing to enhance both electronic and ionic transport.

Table 5-1. The effect of mixing on electrode transport properties.

<table>
<thead>
<tr>
<th>CBD cluster size (um)</th>
<th>Electronic conductivity (mS/cm)</th>
<th>$N_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3228</td>
<td>5.3</td>
</tr>
<tr>
<td>8</td>
<td>3065</td>
<td>6.5</td>
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</table>
6 REFERENCES


16. Lithium Ion Fires & Explosions are Preventable; Available From: http://priusblack.blogspot.com/2016/09/lithium-ion-fires-explosions-are.html.


37. Habte, B.T. and F. Jiang, Microstructure reconstruction and impedance spectroscopy study of LiCoO2, LiMn2O4 and LiFePO4 Li-ion battery cathodes. Microporous Mesoporous Materials, 2018. 268: p. 69-76.


46. Song, Z., Modeling and Simulation of Heat of Mixing in Li-Ion Batteries. 2015, Purdue University: Master's thesis.


55. Schmitt, M., Slot die coating of lithium-ion battery electrodes. 2016: KIT Scientific Publishing.


60. Primo, E.N., M. Chouchane, M. Touzin, P. Vázquez, and A.A. Franco, Understanding the calendering processability of Li (Ni0.33Mn0.33Co0.33) O2-based cathodes. Journal of Power Sources, 2021. 488: p. 229361.


79. Ngandjong, A.C., T. Lombardo, E.N. Primo, M. Chouchane, A. Shodiev, O. Arcelus, and A.A. Franco, Investigating electrode calendering and its impact on electrochemical


88. Bryant Polzin, personal communication based on data collected at Argonne National Laboratory, 01/06/2021.


120. Stamps, M.A., Jeffrey W. Eischen, and Hsiao-Ying Shadow Huang, Particle-and crack-size dependency of lithium-ion battery materials LiFePO4. AIMS Mater. Sci, 2016. 3.1 p. 190.


