The Effect of Microstructure On Transport Properties of Porous Electrodes

Serena Wen Peterson
*Brigham Young University - Provo*

Follow this and additional works at: [https://scholarsarchive.byu.edu/etd](https://scholarsarchive.byu.edu/etd)

Part of the [Chemical Engineering Commons](https://scholarsarchive.byu.edu/etd)

**BYU ScholarsArchive Citation**


[https://scholarsarchive.byu.edu/etd/4431](https://scholarsarchive.byu.edu/etd/4431)

This Dissertation is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of BYU ScholarsArchive. For more information, please contact scholarsarchive@byu.edu, ellen_amatangelo@byu.edu.
The goal of this work is to further understand the relationships between porous electrode microstructure and mass transport properties. This understanding allows us to predict and improve cell performance from fundamental principles. The investigated battery systems are the widely used rechargeable Li-ion battery and the non-rechargeable alkaline battery. This work includes three main contributions in the battery field listed below.

**Direct Measurement of Effective Electronic Transport in Porous Li-ion Electrodes.** An accurate assessment of the electronic conductivity of electrodes is necessary for understanding and optimizing battery performance. The bulk electronic conductivity of porous LiCoO$_2$-based cathodes was measured as a function of porosity, pressure, carbon fraction, and the presence of an electrolyte. The measurements were performed by delamination of thin-film electrodes from their aluminum current collectors and by use of a four-line probe.

**Imaging and Correlating Microstructure To Conductivity.** Transport properties of porous electrodes are strongly related to microstructure. An experimental 3D microstructure is needed not only for computation of direct transport properties, but also for a detailed electrode microstructure characterization. This work utilized X-ray tomography and focused ion beam (FIB)/scanning electron microscopy (SEM) to obtain the 3D structures of alkaline battery cathodes. FIB/SEM has the advantage of detecting carbon additives; thus, it was the main tomography tool employed. Additionally, protocols and techniques for acquiring, processing and segmenting series of FIB/SEM images were developed as part of this work. FIB/SEM images were also used to correlate electrodes’ microstructure to their respective conductivities for both Li-ion and alkaline batteries.

**Electrode Microstructure Metrics and the 3D Stochastic Grid Model.** A detailed characterization of microstructure was conducted in this work, including characterization of the volume fraction, nearest neighbor probability, domain size distribution, shape factor, and Fourier transform coefficient. These metrics are compared between 2D FIB/SEM, 3D FIB/SEM and X-ray structures. Among those metrics, the first three metrics are used as a basis for SG model parameterization. The 3D stochastic grid (SG) model is based on Monte Carlo techniques, in which a small set of fundamental inter-domain parameters are used to generate structures. This allows us to predict electrode microstructure and its effects on both electronic and ionic properties.

Keywords: Li-ion battery, alkaline battery, electronic conductivity, microstructure, FIB/SEM, stochastic grid model
ACKNOWLEDGMENTS

I am thankful for my advisor, Dr. Wheeler, and for his guidance and invaluable constructive criticism during my research projects, and especially for his forgiveness and life lessons about how to be an upright person. He also made me a better writer. Without his supervision and support, this dissertation would not have been possible.

I would like to express appreciation to Professors John Harb, Randy Lewis, Thomas Fletcher, and William Hecker for serving as my committee members, and for their comments in my yearly progress meetings. I would also like to thank Rita Fan for collecting some of the experimental data; and Danilo Bustamante and William Lange for their help with image processing.

I would also like to thank all of my family members and friends who supported me and incented me to strive towards my goal. Your prayers for me have sustained me thus far. Finally, I would like to thank my husband, Brandon Peterson, for his love, kindness and the support he has shown me, which has carried me through as I finalized this dissertation.

This work was supported by the Batteries for Advanced Transportation Technologies (BATT) program of the U.S. Department of Energy.
# Contents

1 Introduction .................................................. 1  
  1.1 Motivation of The Work ................................. 1  
  1.2 Scope of The Work ...................................... 2  
  1.3 Outline .................................................. 4  

2 Background .................................................. 7  
  2.1 Electrochemistry ........................................ 7  
    2.1.1 Li-ion Battery ...................................... 7  
    2.1.2 Alkaline Battery ................................... 8  
  2.2 Microstructure .......................................... 9  
    2.2.1 Electrode Microstructure .......................... 10  
    2.2.2 Optimal Structure .................................. 13  
  2.3 Battery Modeling ........................................ 16  
    2.3.1 1D Newman Model .................................. 16  
    2.3.2 Monte-Carlo Type Model ............................ 17  
    2.3.3 Molecular Dynamics Type Model .................... 17  
  2.4 Conclusion ............................................... 18  

3 Electronic Conductivity Of Li-ion Battery Cathodes ....... 19  
  3.1 Introduction ............................................. 19  
  3.2 Sample Preparation ....................................... 21  
    3.2.1 Cathode Fabrication ................................ 21
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.2 Cathode Delamination</td>
<td>22</td>
</tr>
<tr>
<td>3.2.3 Cathode Fabrication Improvements</td>
<td>24</td>
</tr>
<tr>
<td>3.3 Four-Line Probe</td>
<td>27</td>
</tr>
<tr>
<td>3.3.1 Probe Reliability</td>
<td>29</td>
</tr>
<tr>
<td>3.3.2 Cathode Stability</td>
<td>30</td>
</tr>
<tr>
<td>3.4 Results and Discussion</td>
<td>31</td>
</tr>
<tr>
<td>3.4.1 Electronic Conductivity vs. Porosity</td>
<td>31</td>
</tr>
<tr>
<td>3.4.2 Electronic Conductivity vs. Pressure</td>
<td>34</td>
</tr>
<tr>
<td>3.4.3 Electrolyte Effect</td>
<td>35</td>
</tr>
<tr>
<td>3.4.4 Electronic Conductivity of Laboratory-made Cathodes</td>
<td>39</td>
</tr>
<tr>
<td>3.4.5 Carbon and Binder Domain</td>
<td>40</td>
</tr>
<tr>
<td>3.5 Conclusion</td>
<td>44</td>
</tr>
<tr>
<td>4 Imaging</td>
<td>45</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>45</td>
</tr>
<tr>
<td>4.2 Image Tomography</td>
<td>45</td>
</tr>
<tr>
<td>4.2.1 X-ray Tomography</td>
<td>46</td>
</tr>
<tr>
<td>4.2.2 FIB/SEM</td>
<td>47</td>
</tr>
<tr>
<td>4.2.3 Application</td>
<td>48</td>
</tr>
<tr>
<td>4.3 Acquiring Image Series</td>
<td>50</td>
</tr>
<tr>
<td>4.4 Image Pre-processing</td>
<td>54</td>
</tr>
<tr>
<td>4.4.1 Image Alignment</td>
<td>54</td>
</tr>
<tr>
<td>4.4.2 Image Stretching</td>
<td>54</td>
</tr>
<tr>
<td>4.4.3 Image Cropping</td>
<td>55</td>
</tr>
<tr>
<td>4.4.4 Correction of Image Defects</td>
<td>56</td>
</tr>
<tr>
<td>4.5 Image Segmentation</td>
<td>58</td>
</tr>
<tr>
<td>4.5.1 Manual Segmentation</td>
<td>59</td>
</tr>
<tr>
<td>4.5.2 Computer Segmentation</td>
<td>60</td>
</tr>
</tbody>
</table>
6.2 Background .......................................................... 126
  6.2.1 Probability vs. Energy ...................................... 127
  6.2.2 Previous Algorithms ........................................ 128
6.3 Algorithm Improvement ............................................ 130
  6.3.1 Input and Output ............................................. 130
  6.3.2 Particle-Size Enforcement ................................. 131
  6.3.3 Tip-Growth Move ............................................. 135
  6.3.4 Termination .................................................. 137
6.4 Model Results and Discussion ................................. 138
  6.4.1 Model Validation ............................................. 138
  6.4.2 3D vs. 2D Input ............................................. 140
  6.4.3 BNB90 vs. MX15 ............................................ 141
  6.4.4 BNB90 Fraction .............................................. 143
6.5 Model Prediction .................................................. 146
  6.5.1 Morphology ................................................... 146
  6.5.2 Cell-Level Simulation ..................................... 148
6.6 Conclusion .......................................................... 151

7 Correlating Microstructure To Conductivity .................. 153
  7.1 Introduction ..................................................... 153
  7.2 Measurements of Conductivity ............................... 153
  7.3 Measurements of Microstructures ............................ 155
    7.3.1 Expanded Graphite ....................................... 156
    7.3.2 Non-expanded Graphite .................................. 158
    7.3.3 Fiber Mixture ............................................. 160
  7.4 Wet Cathodes .................................................... 162
  7.5 Conclusion ........................................................ 167
8 Summary and Scope of Future Work 169

8.1 Summary of Results .................................................. 169
8.2 Future Work .......................................................... 171
  8.2.1 Model .............................................................. 172
  8.2.2 Experiment ....................................................... 172

A Manual for Li-ion Battery Cathode Fabrication 185

B Tutorial for Taking Series of FIB/SEM Images 191

C Program Scripts ....................................................... 197
  C.1 Stretch and Alignment (Matlab) ................................. 197
  C.2 Image Segmenting (Matlab) ..................................... 199
  C.3 Compute Conductivity of 3D Structure (FORTRAN) ........ 201
  C.4 Stochastic Grid Model (FORTRAN) ........................... 203
# List of Figures

1.1 Scope of work ......................................................... 3

2.1 Cross-sectional view of battery cathodes .......................... 9

2.2 Schematic of a representative battery cathode ...................... 10

2.3 FIB/SEM images of lithium ion battery cathode ................... 11

2.4 FIB/SEM images of alkaline battery cathodes ..................... 12

2.5 EMD morphology. .................................................... 13

2.6 Illustration of transport properties in parallel or series structures .... 14

3.1 EDX of Li-ion cathode after gallium delamination ............... 24

3.2 EDX of Li-ion cathode after concentrated KOH delamination .... 25

3.3 Image of four-line probe ........................................... 28

3.4 Electronic conductivity of dry commercial LiCoO$_2$ films with porosity .... 32

3.5 FIB/SEM images of commercial cathode at 45%, 34% and 25% porosity ... 33

3.6 The effect of pressure on electronic conductivity of LiCoO$_2$ cathodes .... 34

3.7 The effect of solvent on electronic conductivity of LiCoO$_2$ cathodes .... 37

3.8 Electronic conductivities of laboratory-made baseline cathodes .......... 39

3.9 The effect of carbon fraction on electronic conductivity of Li-ion battery. .... 42

3.10 FIB/SEM images of different carbon weight percentages of cathodes .... 43

4.1 Schematic of image tomography. .................................... 47

4.2 Tomography scale mapping. ........................................ 49

4.3 Preparation steps illustration for FIB/SEM series of imaging .......... 51
5.12 FIB/SEM image of segmented BNB90 and graphene cathodes. . . . . . . . . 106
5.13 Fourier correlation vs. wave number of BNB90 and graphene cathodes . . . . 107
5.14 Illustration of finite volume method. . . . . . . . . . . . . . . . . . . . . . . 111
5.15 Model validation with a dummy structure. . . . . . . . . . . . . . . . . . . . . . 113
5.16 3D microstructures of electrodes for conductivity computation. . . . . . . . . 115
5.17 Coarse-Grain effects on effective conductivity computation. . . . . . . . . . 119
5.18 Effective conductivity sensitivity of domain intrinsic conductivity. . . . . . . 121

6.1 3D SG model configuration visualization. . . . . . . . . . . . . . . . . . . . . . 131
6.2 Illustration of carbon domain connecting algorithm. . . . . . . . . . . . . . . . . 132
6.3 Model configuration comparison before and after particle size enforcement. . 135
6.4 Segmented FIB/SEM image vs. model configuration. . . . . . . . . . . . . . . . 136
6.5 Model configuration termination . . . . . . . . . . . . . . . . . . . . . . . . . . . 138
6.6 SG model validation: model configuration vs. 3D FIB/SEM structure. . . . . 139
6.7 2D FIB/SEM vs. 3D FIB/SEM as input for SG model configuration. . . . . . . 140
6.8 FIB/SEM vs. model microstructure for BNB90 and MX15 cathodes. . . . . . 142
6.9 Segmented FIB/SEM images for various BNB90 mass fraction cathodes. . . 144
6.10 Domain volume fractions of pellets with different BNB90 weight percentages. 145
6.11 Transport property of BNB90 weight percentages: SG model vs. experiment. 146
6.12 Predicted SG model configurations of diverse domain morphology. . . . . 147
6.13 Alkaline battery potential vs. time at 1 A and 0.25 A discharge. . . . . . . 150
6.14 Cell potential vs. time for various ionic conductivities. . . . . . . . . . . . . 151

7.1 Conductivities for various carbon additives. . . . . . . . . . . . . . . . . . . . . 155
7.2 Porosity of different carbon additive cathodes prepared at pressure (54 psi). . 156
7.3 FIB/SEM images for expanded graphite cathodes. . . . . . . . . . . . . . . . . 157
7.4 Magnified cathode of BNB90 abundant and deficient region. . . . . . . . . . . 158
7.5 FIB/SEM images of four non-expanded graphite cathodes. . . . . . . . . . . 159
7.6 FIB/SEM images of graphene and KS15 cathodes. .......................... 160
7.7 FIB/SEM images for nanofiber mixture cathodes. ...................... 161
7.8 Cross section of nanofiber mixture cathodes. ............................. 163
7.9 FIB/SEM images of wet BNB90 cathodes. ................................. 164
7.10 EDAX analysis of dried out commercial alkaline battery cathode. .... 165
7.11 FIB/SEM image of dry and dried out commercial cathode. .......... 166

A.1 Li-ion cathode fabrication spreadsheet. ................................. 186
A.2 Gallium delamination setup. ............................................. 188

B.1 Interface of the Helios Nanolab 600. ................................. 191
B.2 Illustration of Slice and view software. ............................... 195
List of Symbols

Roman

\( A \) \hspace{1cm} \text{area for a 2D structure and surface area for a 3D structure}

\( a \) \hspace{1cm} \text{the surface area per volume}

\( a' \) \hspace{1cm} \text{the perimeter per area}

\( C_{ij} \) \hspace{1cm} \text{Fourier correlation of domains } i \text{ and } j

\( D \) \hspace{1cm} \text{diffusivity}

\( DSD \) \hspace{1cm} \text{domain size distribution}

\( dy, dy' \) \hspace{1cm} \text{height of image}

\( E_{ij} \) \hspace{1cm} \text{direct pairwise potential energy}

\( F(k) \) \hspace{1cm} \text{Fourier transformation}

\( F^*(k) \) \hspace{1cm} \text{complex conjugate of } F(k)

\( f(r_j) \) \hspace{1cm} \text{dimensionless Fourier coefficient (value is 1 or 0)}

\( g_{ij} \) \hspace{1cm} \text{normalized nearest-neighbor probabilities}

\( G_i(s_I) \) \hspace{1cm} \text{relative probability of site } I \text{ containing domain } i

\( I \) \hspace{1cm} \text{current}

\( i \) \hspace{1cm} \text{imaginary number}
**k** reciprocal lattice vector

**$k_B$** Boltzmann constant

**$k_{ij}$** harmonic mean for conductivities of domains $i$ and $j$

**$L$** length or height of electrode

**$m$** mass

**$n$** number of observations of the sample

**$N$** number of pixels or voxels

**$X$** location vector

**$I^{(i)}(X)$** the function for $X$ belonging to phase $i$

**$P$** perimeter

**$P_{ij}$** node-to-node (pixel or voxel) contact probabilities

**$P_{I \rightarrow J}$** transition probability function

**$P(x_n)$** new configuration probability

**$P(x_o)$** old configuration probability

**$P_{ij}^{L}$** lateral nearest neighbor probabilities

**$P_{ij}^{D}$** diagonal nearest neighbor probabilities

**PSD** particle size distribution

**$r$** distance between two voxels

**$r_i$** radius of particles

**r** position vector
\( s \)  the standard deviation of all samples

\( S \)  area of electrode cross-section

\( S_{IJ} \)  unit direction vector between voxels \( I \) and \( J \)

\( t \)  \( t \) value at \( t \) table of the Student’s \( t \) distribution

\( T \)  temperature

\( \Delta V \)  voltage drop

\( V \)  volume

\( v \)  volume fraction

\( w_{ij} \)  potential of mean force

\( w \)  electrode constituent mass fraction

\textbf{Greek}

\( \alpha \)  empirical exponent

\( \delta \)  node size

\( \epsilon \)  nano porosity

\( \varepsilon \)  macro porosity

\( \kappa \)  ionic conductivity

\( \rho \)  density of an electrode constituent

\( \sigma \)  electronic conductivity

\( \sigma_0 \)  electrode conductivity at zero porosity
\( \tau \)  tortuosity

\( \nabla \phi \)  potential field

\( \chi \)  porosity at which \( \sigma \) is about half of \( \sigma_0 \) value

\( \omega \)  frequency

**Subscripts**

\( i, j \)  domain types

\( I \)  center site

\( J \)  adjacent site

max  maximum

min  minimum

**Superscripts**

eff  effective

ext  external

dev  deviation

tot  total
Chapter 1
Introduction

1.1 Motivation of The Work

Batteries are attracting increasing amounts of attention as an energy solution. Batteries in portable electronics like cell phones and laptops are relatively mature technologically and reasonably priced for those applications. However, the promising emerging battery markets in electric vehicles (EVs) and grid storage systems face some challenges [1–4]. In order to bring these compelling technologies to market, batteries must exhibit low prices, long life, high specific energy, safe operation and minimal maintenance. In addition, batteries must work in hot and cold temperatures, deliver high power on demand and charge quickly. Further work on cost-effective and high-performance batteries will potentially bring great commercial benefit.

An augmented understanding of manipulating porous structures to improve macroscopic transport properties (electronic and ionic) is valuable for battery advancement [5]. For example, a cell with thicker electrodes tends to have higher specific energy, but suffers from power loss, or low specific power levels. Such a cell contains a small fraction of inert components and thus more reactive material per kilogram. However, because ions and electrons have a longer way to travel through the electrode, transport losses increase and specific power is reduced. Similarly, decreasing electrode thickness may enhance cell power, but the relative increase of inactive components such as separators and packaging decreases gravimetric and
volumetric energy density. In addition to optimizing the thickness of battery electrodes, eco-
nomic and superior batteries with high discharge capabilities and energy density will require
the development of improved porous electrode microstructures [6].

This work is part of a larger effort to study the relationship between fabrication parama-
ters, electrode microstructure, and cell properties. The connection between structure and its
transport properties is not fully understood. Potential contributions of this research include
lower-cost cell manufacturing and higher cell performance.

1.2 Scope of The Work

This project focuses on understanding how cathode microstructure affects electronic and
ionic resistances, and how to optimize microstructure through improved fabrication pro-
cesses to yield higher performance. We particularly seek to answer the following questions:
What practical microstructures facilitate high performance? For example, what effect do
composition and morphology have on transport property performance? Specifically, how do
electronic and ion conductivity change as these variables change?

Transport properties include electronic and ionic conductivity. There are trade-offs be-
cause electrons and ions generally transport through distinct phases that cannot occupy
the same volume. Furthermore, most of the active materials in batteries are only semi-
conductive, and as such require some conductive additives such as carbon to carry electrons
[2]. Carbon particles provide electron pathways across the electrode but also can obstruct
pores that are the pathways for ions [7].

As shown in Fig. 1.1, connections between cell microstructure and transport properties
can be made using a combination of experiments and models. This work is organized into
three divisions.

First, in order to better quantify macroscopic transport properties and understand the
trade-offs between electronic and ionic conductivity, it is crucial to develop experiments
Figure 1.1: Scope of this work showing connections between microstructure and transport properties using a combination of experiments and models.

that enable us to directly measure these two transport properties separately. Experimental apparatuses are developed for directly measuring electronic and ionic conductivity. These conductivities are measured for a variety of sample electrodes.

Second, experimentally obtaining battery electrode microstructures allows us to compute macroscopic transport properties based on 3D electrode microstructures. Images of electrodes are formed into a 3D electrode microstructure from which we can compute macroscopic transport properties by solving transport equations on 3D grids. Images of electrode microstructure provide raw-material spatial information which is used to parametrize a 3D microstructure model.

Lastly, developing a 3D microstructure model permits simulation and prediction of electrode microstructure and transport properties without experimental trials. This model is called the stochastic grid (SG) model and is based on Monte Carlo simulation methods (voxel swap). The SG model uses spatial information from imaging to parametrize a modeling configuration, which is compared to 3D experimental microstructures. As with experimental structures, we can compute the transport properties of each model configuration. Further, models allow us to simulate as-yet-unrealized cell configurations, which can provide more insights on how microstructure could possibly affect macroscopic transport properties.
1.3 Outline

Two commercially important battery systems, Li-ion and alkaline, are investigated with a focus on the respective cathodes. Due to the changing sources of our funding, projects alternate between the two battery systems. In some cases, one tool is used only for Li-ion or alkaline batteries, but the lesson learned is applied to both systems. The remainder of this document is organized as follows:

Background. Chap. 2 is a brief description of the electrochemistry and microstructure of the investigated battery systems, including Li-ion and alkaline batteries. This chapter also reviews two main simulation methods for modeling battery microstructure.

Electronic Conductivity Of Li-ion Battery Cathodes. Chap. 3 describes the electronic conductivity of electrodes using a four-line probe developed in our laboratory. It is important to directly measure the electronic conductivity of Li-ion battery cathodes in order to understand and optimize battery performance. The bulk electronic conductivity of porous LiCoO$_2$-based cathodes is measured as a function of porosity, pressure, carbon fraction, and the presence of an electrolyte. Most of the content of this chapter has been published previously in the Journal of the Electrochemical Society [8].

Imaging. Chap. 4 shows a few imaging techniques used to obtain 3D microstructures of porous electrodes for Li-ion and alkaline batteries. This chapter covers image acquisition, image segmentation, and 3D structure reconstruction and visualization. The 3D microstructure of alkaline battery cathodes is presented.

Electrode Microstructure Metrics. Chap. 5 presents metrics to describe the microstructure of battery electrodes. These metrics include volume fraction, nearest-neighbor probability, particle morphology and Fourier spectrum. Further, the transport properties of 3D microstructures are computed as an additional metric. The conductivity of the 3D structure is compared to experimental conductivity measurements.

Stochastic Grid Model. Chap. 6 describes a 3D microstructure model for alkaline battery cathodes. The stochastic grid (SG) model uses the metrics in Chap. 5 to generate new
configurations which are compared to the 3D structure obtained from Chap. 4. The SG model conductivity simulation results are validated for electrodes with different graphite types and volume fractions. Preliminary SG model prediction results are given for different raw material morphologies.

Correlating Microstructure to Conductivity. Chap. 7 correlates microstructure to conductivity performance for alkaline battery cathodes. The effects of various carbon additives on cathode electronic conductivity are investigated. FIB/SEM (focused ion beam/scanning electron microscope) images are used to correlate the electrode microstructure to electronic conductivity. Parts of this chapter have been published previously in the Journal of the Electrochemical Society [9].

Conclusions. Chap. 8 presents the conclusions drawn from this work as well as some suggestions for future work to be done on the subject of electrode microstructure and transport properties.
Chapter 2
Background

This chapter first reviews the characteristics of the two investigated battery systems, then shows cathode microstructures for each type. In addition, we preliminarily discuss the effects of microstructure. Finally, this chapter covers modeling work in the battery field with a focus on modeling porous electrodes.

2.1 Electrochemistry

Thermodynamics determines battery open circuit potential (OCP). The two electrochemical battery systems used in this study are the leading commercial battery systems. Li-ion is the leading rechargeable battery type, with an OCP of around 4 volts. Alkaline batteries are a well known primary battery system (not rechargeable), and the OCP is around 1.5 volts.

2.1.1 Li-ion Battery

Over the last two decades, lithium-ion batteries have become the leading secondary (rechargeable) battery technology and are widely used in portable electronics and a growing number of electric vehicles [2–4]. The most common Li-ion battery cathode chemistries include lithium cobalt oxide, lithium iron phosphate, lithium manganese oxide, and lithium nickel manganese cobalt oxide. These cells have high energy density (based on weight or volume) primarily because of the high cell voltage [10, 11].
In Li-ion batteries, lithium ions are transported to and from the cathode or anode through a non-aqueous electrolyte and separator. During discharging, the battery reactions are as follows: The anode reaction is

\[ C_n Li_x \rightarrow C_n + x Li^+ + x e^- \quad E_{anode}^o = +0.1 \text{ V} \quad (2.1) \]

The cathode reaction is

\[ Li_{1-x}CoO_2 + x Li^+ + x e^- \rightarrow LiCoO_2 \quad E_{cathode}^o = +3.9 \text{ V} \quad (2.2) \]

The overall cell reaction is obtained by combining the above equations:

\[ Li_{1-x}CoO_2 + C_n Li_x \rightarrow LiCoO_2 + C_n \quad E_{cell}^o = 3.8 \text{ V} \quad (2.3) \]

For charging, an external power supply is needed to force the lithium ions to move back to the anode from the cathode. The electrochemical reactions are the reverse of those listed above.

### 2.1.2 Alkaline Battery

Another electrochemical system is the Zn − MnO₂ system found in primary (non-rechargeable) alkaline batteries, which Georges Leclanché invented in 1868. Alkaline Zn − MnO₂ batteries are still one of the most used battery types. Alkaline batteries consist of a zinc powder gel in the anode and electrolytic manganese dioxide (EMD) in the cathode. EMD is a high activity gamma-MnO₂ with low metallic impurities and desirable electrochemical properties.

During discharge, the zinc is oxidized by a dissolution-precipitation process, while the EMD is reduced by a solid-state intercalation of H⁺ into the EMD lattice [12]. The electrochemical reactions during the discharge process are as follows: The anode reaction is

\[ Zn + 2 OH^- = ZnO + 2 e^- + 2 H_2O \quad E_{anode}^o = -1.36 \text{ V} \quad (2.4) \]
The cathode reaction is

\[
2 \text{MnO}_2 + 2 e^- + 2 \text{H}_2\text{O} = 2 \text{MnOOH} + 2 \text{OH}^- \quad E_{\text{cathode}}^\circ = +0.29 \text{V}.
\] (2.5)

The overall reaction:

\[
2 \text{MnO}_2 + \text{Zn} + 2 \text{H}_2\text{O} = 2 \text{MnOOH} + \text{ZnO} \quad E_{\text{cell}}^\circ = 1.65 \text{V}.
\] (2.6)

### 2.2 Microstructure

In order to understand the relationship between electrode microstructure and transport properties, it is essential to know the microstructural characteristics of the electrode.

All batteries include an anode, separator and cathode. In a battery, to avoid self-discharging due to the electrochemical reactions, a separator layer is required. Separator does not allow electrons to flow directly between anode and cathode, forcing electrons to pass through external wires, and in so doing, provide power to a device. Fig. 2.1 shows

![Cross-sectional views of batteries](image)

Figure 2.1: (a) Cross-sectional cell view of Li-ion battery, (b) cross-sectional cell view of alkaline battery. Images are adapted from [13, 14].
cross-sectional cell views of Li-ion and alkaline batteries. These battery systems are designed differently in terms of manufacturing. In a Li-ion battery (a), the anode, separator and cathode are thin, stacked layers which are rolled together in the battery can. Alkaline batteries (b) are manufactured in a tubular fashion. EMD is mixed with graphite and a small amount of KOH and formed into granulate, then the granulates are pressed into pellets with a die. Cathode pellets are placed into a stainless steel can, then the separator and zinc slurry are added.

2.2.1 Electrode Microstructure

This work focuses on battery cathodes. The cathodes of Li-ion and alkaline batteries have certain similarities. Fig. 2.2 shows a schematic diagram of a porous, particle-based cathode. Both types of cells discussed above are composed of active material, carbon additive, and void or pores. The presence of a carbon additive is mainly to reduce electronic resistance, since the active material often has low electronic conductivity. The electrons hop between particles while ions pass through the void phase. The electrochemical reaction takes place on the particle surfaces.

Figure 2.2: Schematic of a representative battery cathode. Green represents active material particles, black represents carbon additives, and white represents pore space.

A long service life (high capacity) is desirable for a cell; however, cell sizes have often been fixed. High capacity means greater amounts of electrode active materials (green particles in Fig. 2.2) in the cell, which is of fixed size. This is usually achieved by decreasing the
amount of non-electrochemically active materials such as the conductive additive. However, a sufficient quantity of conductive additive must be maintained to ensure an adequate level of bulk conductivity in the cathode. Therefore, there is a need to optimize the microstructure to meet the demands of various battery applications.

**Li-ion Battery Cathodes** Fig. 2.3 (a) shows the cross-section of a commercial Li-ion battery cathode. Part (b) shows an enlargement of the carbon domain microstructure, which is an aggregation of carbon black particles and binder. The approximate thicknesses or sizes of the cathode film, active material particles, and carbon black particles are 100 µm, 15 µm, and 50 nm, respectively. The median size of the active material particles is much larger than the carbon black particles. The differences in particle size present challenges when constructing models of cathode microstructure [15, 16]. As we observed in part (b), carbon black and binder aggregate to form the carbon domain, which exhibits size similar to the active material LiCoO$_2$ [7].

![FIB/SEM images of lithium ion battery cathode](image1)

Figure 2.3: (a) FIB/SEM images of lithium ion battery cathode, (b) enlargement of region in black box, showing the carbon domain microstructure.

**Alkaline Battery Cathodes** Fig. 2.4 shows cross-sectional images of commercial alkaline battery cathodes made by (a) Duracell and (b) Energizer. Parts (c) and (d) are enlarged
Figure 2.4: FIB/SEM images of alkaline battery cathodes: Duracell Coppertop (a) and Energizer Max AA (b). Panels (c) and (d) are enlarged views of (a) and (b), respectively. Dark gray is carbon additive (graphite) and light gray is EMD.

views of (a) and (b), respectively. The gray and dark gray phases are electrolytic manganese dioxide (EMD) and carbon additive (graphite), respectively. Graphite not only assists electron flow but also acts as a lubricant and binder in alkaline batteries. The approximate or characteristic sizes for the cathode, active material, and graphite are 1 cm, 40 μm, and 5 μm, respectively [17].

EMD as an active material for alkaline batteries has a large amount of fine cavities [18–20], which provide sizable locations for reaction. Fig. 2.5 (a) is a surface view of EMD particles. It makes evident the large particle size distribution and aspect ratio. Part (b) is
Figure 2.5: (a) Surface view of EMD particles, (b) cross section view (FIB/SEM) of pure EMD pellet, (c) magnified features of red boxes, (d) magnified features of yellow box.

a cross section (FIB/SEM) of a pure EMD pellet after high compression. Parts (c) and (d) magnify the features in the boxed regions in part (b), showing evidence of pores in EMD particles.

### 2.2.2 Optimal Structure

Many efforts have been devoted to making batteries with superior structure [21, 22]. Electron and ion sources are located on opposite sides of the electrode. The optimal structures for electronic and ionic transport are hierarchical pathways frequently observed in natural
systems such as the vascular system in trees [21–23]. One could emulate such vascular structures to transport ions and electrons in batteries [24–26], but it would take tremendous manufacturing effort and is not currently economical. To do so, one way to achieve optimal design is to use deterministic 3D fabrication techniques [21, 27–29]. For instance, Golodnitsky developed thin-film cathodes for application in 3D micro batteries [30]. Goldman used 3D hierarchically patterned single-crystal silicon microstructures as high-energy-density anodes in lithium-ion batteries [31]. These two studies showed an increase in the capacity and energy density of the cell. However, the complex geometries of 3D micro electrodes require precise fabrication controls and multiple steps. Thus, the issue of cost also limits scale up of these technologies for industry.

Figure 2.6: Illustration of transport properties in parallel or series structures, where direction 1 (Dir 1) is in parallel, whereas direction 2 (Dir 2) is in series. Blue, green, and red represent pore (10%), active material (80%), and carbon additive (10%), respectively.

Instead of developing complex and highly controlled microstructures, a fruitful approach is to investigate the effect of relatively small changes to particle-based morphologies on
battery performance. Fig. 2.6 shows the potential transport property difference that microstructure can make. We can analyze the theoretical limits (lower and upper bounds) on the effective conductivity of composites. Suppose the three phases blue, green, red represent pore (10%), active material (80%), and graphite (10%), respectively. Assuming the current flows along direction 1, the three phases are in parallel, so the overall conductivity is maximized as shown by Eq. 2.7:

\[ \sigma_{\text{max}} = v_A \sigma_A + v_P \sigma_P + v_C \sigma_C \]  

(2.7)

In direction 2, the three phases are in series, so the overall conductivity is minimized as shown by Eq. 2.8:

\[ \frac{1}{\sigma_{\text{min}}} = \frac{v_A}{\sigma_A} + \frac{v_P}{\sigma_P} + \frac{v_C}{\sigma_C}, \]  

(2.8)

where \( v_i \) indicates the volume fractions and \( \sigma_i \) represents electronic conductivities. If we use alkaline batteries as an example, for electronic conductivity, \( \sigma_P \) is zero, \( \sigma_{\text{EMD}} \) is around 0.5 S cm\(^{-1}\) and \( \sigma_C \) is about \( 10^5 \) S cm\(^{-1}\) (for more detail, see Sec. 5.5.1). Thus, the conductivity for this configuration has extremely isotropic properties depending on the direction of current flow. The maximum electronic conductivity \( \sigma_{\text{max}} \) would be around \( 10^4 \) S m\(^{-1}\), whereas the minimum \( \sigma_{\text{min}} \) is only a single-digit value.

According to this analysis, there is room for improvement through changes to the microstructure of traditional batteries. Some of the main factors affecting microstructure such as volume ratios, surface areas, particle size and shape are investigated in some studies [7, 32–34]. However, there are many possibilities which can be more thoroughly investigated in order to quantify these variables’ effects on performance.
2.3 Battery Modeling

Outside of our group, few studies have been done to predict the 3D microstructure of porous electrodes; rather, most related studies have worked on the reconstruction of 3D electrodes and the analysis of segmented 3D electrodes [32, 35, 36]. Sastry and coworkers have explored models based on a random packing of spherical or ellipsoidal particles [37, 38]. Our group studied the relationships between microstructure and ionic transport properties from a predicted 3D microstructure model of a LiCoO$_2$ cathode [7]. This section reviews modeling work in macro-level (homogeneous) battery models and two types of electrode microstructure models, namely, a Monte-Carlo type model and a molecular dynamic type model.

2.3.1 1D Newman Model

Battery modeling efforts have often relied on the application of spatially averaged electrode transport and reaction parameters. Most notably, Newman et al. [39] developed early models based on one-dimensional transport across battery components. This type of model assumes that the electrode is an isotropic, homogeneous, material constructed from mono-dispersed (spherical and with uniform size) particles. This simplification greatly decreases numerical costs.

In the last few years, Comsol has been used to implement 1D Newman model simulations to optimize electrode properties such as film thickness and porosity [40]. However, the 1D model itself cannot predict the effect of microstructure changes such as volume fractions and phases interaction. To get effective (volumetrically averaged) transport parameters, one must perform experiments or use a predictive 3D microstructure model. Therefore, developing a 3D electrode microstructure model could predict effective transport properties for macro-level battery models without conducting experiments.
2.3.2 Monte-Carlo Type Model

Monte-Carlo simulation has been used in statistical physics for many decades. Our group adapted it to the three-phase battery electrode model [7]. The Monte-Carlo (MC) type model divides the electrode into many nodes on a grid, each representing a small volume that can be occupied by active material, carbon or pore. It is based on the MC numerical method and node swapping techniques [41, 42].

A core step of the MC type model is called the Metropolis algorithm, in which a swap between randomly selected nodes is accepted or rejected based on the relative probabilities of the initial and proposed configurations. When a swap is made, the phase identities of the two nodes are exchanged. The microstructure evolves as many swaps are attempted and made. This node swap technique naturally conserves the volume fraction of each phase.

The MC type model tends to drive toward a thermodynamic equilibrium configuration, which in practice leads to a minimum surface area between domains. In reality, the shape of the solid active material is not governed by thermodynamic equilibrium, while carbon domain shapes are more likely to be governed by thermodynamic equilibrium. In order to partially fix this discrepancy, David Stephenson interrupted the simulation before it reached equilibrium. The algorithm determines the best step at which to stop by evaluating how well the domain contact probabilities match those from the FIB/SEM cross section image [7].

In summary, the previous MC type model has some physical basis but remains a poor descriptor of active material particle shapes due to the nature of the Metropolis algorithm, which seeks a minimum system free energy. As part of this work, several algorithms are added to improve the results, as discussed in Chap. 6.

2.3.3 Molecular Dynamics Type Model

The MD method was originally designed for molecular-level modeling and handling many particles, but it can be adapted to mesoscale systems [40, 43]. The molecular dynamic (MD) type model predicts microstructure by simulating real particles interacting inside a fixed
volume representing an electrode. This model calculates the particle forces, velocities, and positions as functions of time. The DPP model allows for simulation of electrode fabrication process, but there is no direct connection between pixelated image metrics and DPP model parameters. A 3D mesoscale model of the collector-electrode interface in Li-ion batteries was developed using a dynamic collision algorithm [43].

Using DPP, it is hard to obtain shaped particles or domains. Initial trials were attempted in our group to predict electrode microstructure using the MD type model, which is based on aggregates of spheres that move collectively in response to inter-particle forces [7]. Using this model as implemented, it was hard to conserve the volume fraction of each particle domain. The model also failed to accurately describe particle shapes using only interactions between spheres.

2.4 Conclusion

Although Li-ion and alkaline batteries have different electrochemistries and macroscopic cell characteristics (cathode sizes and packing methods), both systems’ cathode microstructures have three phases: active material, carbon additive, and pore. The domain sizes of these two types of cathodes are different: alkaline batteries have domains from 1-50 micrometers, while for the investigated Li-ion battery system domains are around 5-15 micrometers. In addition, compared to Li-ion batteries, the three phases in alkaline batteries have highly irregular shapes. These differences between the two cathode types pose different challenges to conductivity measurement, imaging, and developing an electrode model. These challenges are addressed in the following chapters.

There are two main modeling methods that are used to generate porous structure, namely, the Monte-Carlo (MC) and Molecular Dynamic (MD) methods [44–49]. The MC method swaps node identities according to statistical preference. The MC method is used in this work, while one of my colleagues is further developing the MD electrode model.
Chapter 3
Electronic Conductivity Of Li-ion Battery Cathodes

3.1 Introduction

Electronic and ionic conductivities have a significant effect on the performance of Li-ion battery materials [2]. The cathode, the focus of this work, is a major determinant of the energy density, rate capability and cost of Li-ion batteries [50, 51]. Our research group has investigated and modeled the trade-off between electronic and ionic transport properties within porous cathodes [7, 52, 53]. Carbon particles in the cathode provide electron pathways but can also obstruct pores that are the pathways for ions. It is important that electrical and ionic conductivities are optimized in the cathode, since either of these values can limit overall cell performance. The work described here can be considered a companion to previous work at BYU, which directly measured effective ionic transport in porous Li-ion electrodes [53].

Effective electronic conductivity data for common Li-ion battery cathodes are also needed for cell performance [53, 54], but such data are often not fully explored in published research. Park et al. [2] reviewed electrical conductivity studies of the major Li-ion cathode active materials in pellet and single-crystal forms, including LiCoO$_2$, LiMn$_2$O$_4$, and LiFePO$_4$. However, in actual electrodes, the cathode particles are in contact with the binder as well as conductive additives [55]. Thus, the effective electronic conductivities of composite electrodes are likely much different from those of pelleted pure active materials.
Developing reliable and robust experimental techniques that can directly measure electronic conductivity is a challenge. Two common techniques for characterizing battery transport properties are electrochemical impedance microscopy (EIS) and the four-point probe [2, 56, 57]. Although EIS delivers quick results, it is difficult to separate electronic and ionic resistances using this method in the presence of an electrolyte [58, 59]. One could perhaps experimentally manipulate electrolyte concentration and then extrapolate pure electronic conductivity using EIS results. However, directly measuring the effective electronic conductivity of porous Li-ion cathodes is more reliable than inferring this property from an experiment that combines multiple modes of charge transport.

The four-point probe technique uses the two outside probes to pass current and the two inside probes to collect a voltage difference. This probe is traditionally used to measure sheet resistance of materials used in the semiconductor. The use of four points of contact allows a correction of the contact resistance between the probes and the tested thin film. However, the four point probe has difficulty maintaining sufficient contact with porous and brittle cathode films without damaging them [60]. In addition, the applied pressure is limited at the four tips of the four-point probe. To correct these deficiencies we use a four-line probe developed in our laboratory. The following sections first introduce the use of a four-line probe to measure the electrical conductivity of electrode films, then report the conductivity of porous LiCoO$_2$-based cathodes as a function of porosity, pressure, carbon fraction, and the presence of an electrolyte. Most of the content of this chapter has been published in the Ref. [8].
3.2 Sample Preparation

Two types of cathodes are examined in this study: commercial and laboratory-made. The commercial cathodes were made under contract by Saft American and are more fully described elsewhere [53]. They have a fixed baseline composition (corresponding to composition 1 in Table 3.1) and were made from a single production run. The cathode roll was then calendered to four different porosities to our specifications. In this study, some of these commercial cathodes were re-calendered in our laboratory to obtain a larger porosity range. The second type of cathode used in this study was fabricated in our laboratory to obtain compositions (shown in Table 3.1) that vary from the baseline composition 1.

Table 3.1: Laboratory-made cathode compositions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Solid (dry wt%)</th>
<th>Added NMP (g/100 g solid)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiCoO₂</td>
<td>PVDF</td>
</tr>
<tr>
<td>Composition 1</td>
<td>94.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Composition 2</td>
<td>90.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Composition 3</td>
<td>86.5</td>
<td>7.5</td>
</tr>
</tbody>
</table>

3.2.1 Cathode Fabrication

The cathode fabrication is based off previous work [53, 58] though some changes were made. The fabrication procedure described here is designed for single-sided LiCoO₂ cathode sheets with a loading of around 14.85 mg cm⁻² active material. This can be compared to the commercial cathodes, which are loaded on both sides of the aluminum current collector and have a loading of 14.85 mg cm⁻² per side.

The fabrication process is as follows: (1) Cut aluminum current collector (25 µm thick, 99% pure) into 14 cm x 15 cm and flatten it on optical flat glass with glass roller. (2) Dissolve PVDF (polyvinylidene fluoride, Kynar 741) in NMP solvent (1-methyl-2-pyrroolidone fluoride) on hot plate with mild heat (80°C) and cover to prevent NMP evaporation. (3) Mix active material LiCoO₂ (Alfa Aesar) and ACB (acetylene carbon black, 100% compressed, Alfa
Aesar) to homogeneity with mortar and pestle for 15 minutes. (4) Add the dry LiCoO$_2$/ACB mixture to the PVDF-NMP solution while the PVDF is totally dissolved. (5) Stir this new mixture with an ultrasonic homogenizer for 15 minutes to achieve a slurry with the desired viscosity. (6) Spread the slurry out onto the flat aluminum sheet with a doctor blade (Byk-Gardner, U.S.A) to the desired thickness (around 200 µm, including the thickness of aluminum current collector, to generate a thickness of dried out cathode around 125 µm). (7) Let the resulting film sit at room temperature for 12 hours, then dry it in a vacuum oven (120°C, 3 kPa) for another 12 hours. (8) Cut the film into 22 mm×22 mm square cathodes, and then the calender square cathodes to the desired porosity. At the completion of this process, the electrodes are ready for delamination, as described below, in order to perform the desired conductivity measurements.

Considerable work was performed to ensure that the laboratory-made electrodes had an electronic conductivity comparable to that of the commercial electrodes, although differences remained, as described below in Sec. 3.4.4. It is crucial to minimize the initial (as-dried) porosity in order to obtain laboratory-made cathodes with porosity around 30% after calendering—that is, too much calendering can damage electrode structure [61]. Various factors were investigated to solve this problem, including cathode material mixing and drying conditions. The final process involved minimizing the amount of NMP solvent (see Table 1) and slowing the drying process as described above.

### 3.2.2 Cathode Delamination

Cathode delamination is used to peel off the current collector from the cathode film, so that the current collector will not affect the conductivity measurement of cathode. This procedure is performed for both the commercial and laboratory-made films using liquid gallium as described in Ref [53], with the following modification. In order to increase the cathode’s mechanical stability during electronic conductivity measurements, the exposed surface of the cut square electrode is adhered to a piece of glass prior to removal of the
current collector. This is done by spraying adhesive (Loctite, spray adhesive, multi-purpose) on the square electrode and gently placing a 22 mm × 30 mm microscope cover glass on top of the sprayed electrode. The exposed aluminum layer is then removed by application of gallium metal at elevated temperature [53]. Two specifics are worth emphasizing: first, pure gallium removes aluminum more successfully than non-purified gallium, so it was quite important to rinse the gallium before reuse. Gallium was heated on the hot plate and rinsed with deionized water. More details are explained in Appendix. A. Second, the dissolving temperature of aluminum with gallium needed to be set around 50°C, because the gallium wouldn’t remove the aluminum if the temperature was too low, while the adhesive would weaken and allow the sample to crack at higher temperatures.

Fig. 3.1 shows the EDX of the cathode after delamination. Parts (a) and (c) are surface views from the top and side of the Li-ion cathode, respectively. The top surface was attached to the aluminum before delamination. The side surface was created after delamination by fracturing the cathode film. Parts (b) and (d) are the corresponding EDX element analyses of (a) and (c). Only a small amount of gallium was detected over a large sample surface shown in part (b). From part (d), it is evident that an insignificant amount of gallium penetrated the cathode.

Another cathode delamination method was attempted using concentrated KOH solution. In a petri dish, 7M KOH solution was added to cover the Li-ion cathode (with the aluminum side up). This concentrated KOH reacts quickly with aluminum, even at room temperature, and produces hydrogen gas. The gas bubbles tend to separate the aluminum foil and cathode as the hydrogen escapes. While this method is a faster way to delaminate aluminum than the previous gallium method, one concern is that the electrode undergoes a chemical or physical change. For instance, it was found that the resulting deliminated cathode had about 100 times higher electronic conductivity than expected values. This may be due to residual metal on the cathode surface. Most of time, we observed some white salt on the cathode surface. Fig. 3.2 part (a) shows the surface of the cathode after KOH delamination. Part (b) is the
Figure 3.1: SEM analysis of Li-ion cathode after gallium delamination: (a) top surface of Li-ion cathode after delamination (this side was attached to the aluminum before delamination), (b) corresponding EDX element analysis of surface (a), (c) side surface view of same Li-ion cathode, (d) corresponding EDX element analysis of (c).

Elemental analysis of the white salt spot marked in part (a). Aluminum and oxygen are detected, so it is likely some mixture of aluminum oxides. The unusually high conductivity may be due to the reaction of KOH with the cathode material, but this has not been proven. Therefore, the concentrated KOH solution delamination method was not used in this study.

3.2.3 Cathode Fabrication Improvements

The porosity of cathodes out of the oven is usually higher than the porosity desired for battery manufacturing. As a result, there is a process of calendering, which compacts particles.
Aggressive calendering, meaning calendering from high to low porosity, is likely to damage cathodes. The bigger the porosity gap before and after calendering, the more challenging it is to obtain good cathodes after the calendering process. Therefore, a lower initial porosity is crucial to successfully obtaining mechanically stable cathodes with a low porosity (around 30%) after calendering. This poses difficulty for cathode fabrication in the laboratory because the previous cathode fabrication recipe resulted in high initial porosity (70%-75%) for the baseline cathode (baseline composition is identical to composition 1 of Table 3.1), and calendering cathode porosity below 50% led to cracking and poor performance [61]. The solvent NMP is the factor which causes a cathode’s porous structure to form, so reducing NMP solvent to the point that the desired porosity can be obtained is a logical step. At the same time, this is a challenge because a sufficient amount of NMP is needed to form a slurry that can be coated on the aluminum.

Various factors were investigated to lower initial porosity, from the cathode material mixing operation, to controlling cathode drying conditions, to optimizing the preparation of the cathode film to be tested. In this instance, the porosity goal was achieved by premixing with mortar and pestle, reducing the amount of solvent (NMP) and decreasing the speed of the drying process. The improved LiCoO$_2$ cathode fabrication recipe is attached in Appendix A.

Figure 3.2: (a) Surface of Li-ion cathode after concentrated KOH delamination (this side was attached to the aluminum before delamination), (b) EDX element analysis of spot area marked with red box in (a).
Premixing with Mortar and Pestle. Using mortar and pestle to pre-mix the active material and carbon additive improved particle distribution and the surface texture of the finished cathodes. Without using mortar and pestle, the surface of the films tended to be more bumpy. This was a problem because it resulted in uneven thickness, which caused the films to crack when calendered. Moreover, the use of mortar and pestle also helped achieve an even distribution of carbon additive throughout the cathode.

Reducing The Amount of Solvent (NMP). Decreasing the amount of NMP greatly reduces initial porosity, bringing it down roughly 10% (from 75% to 65% porosity) for the baseline cathode. NMP solvent is the driving factor in determining initial porous structure because it is the source of pore formation. During the drying process, the NMP evaporates and creates the pores of the electrode film. Based on the attached cathode fabrication recipe, the cathode mixture from step (5) is harder to spread out during step (6) if it has high viscosity resulting from insufficient NMP, while over optimum amounts of NMP create a higher initial porosity. This work optimized the volume of solvent to lower the initial porosity of the electrode while still allowing the slurry from step (5) to spread out.

One method to establish the optimum amount of NMP solvent for different cathode compositions is through identifying the viscosity of slurry in step (5). The present work achieved this by varying the weight ratio of added NMP to solid mix (compositions shown in Table 3.1) and measuring the initial porosity of the resulting cathodes. Specifically, the weight percentage of added NMP to solid mix was decreased at intervals of 15% starting from 125%, which was the percentage used in the previous film fabrication process [61]. The experimental results show that a 56.3% weight percentage of added NMP to solid mix forms a slurry with the desired viscosity for the baseline. Trials were also made to identify the optimum weight ratio for compositions 2 and 3 in Table 3.1.

Decreasing The Speed of Drying Process. One hypothesis to lower initial porosity is to form an electrode structure with densely spaced particles. Initial porosity is strongly
related to the thickness of the electrode cast from step (7). The film thickness as determined by the doctor blade in step (6) is much higher than the film thickness after drying in step (7). This thickness difference comes from NMP evaporation. In our observation, quickly and immediately heating the film from step (7) creates thicker cathodes with greater porosity. Therefore, we instead let the film sit overnight, allowing the particles to settle and form a denser bottom layer while the solvent rose gradually to the surface. Then, the film was gradually heated from room temperature to 120 °C in an oven, so that the solvent evaporated more gradually instead of abruptly drying and forming larger pores. Slowing down the NMP solvent evaporating speed reduced initial porosity by 7% (from 65% to 58%), which was the key step to obtain cathodes with a porosity around 30%.

3.3 Four-Line Probe

The four-line probe technique is an extension of the concept of the four-point probe. In this case, parallel lines are used to contact the sample instead of points. In either case, the use of four points/lines corrects for contact resistance between probe and the sample. Relative to a point probe, a line probe increases the contact area and stability between the probe and the sample. Moreover, our four-line probe allows control and measurement of applied pressure in order to imitate pressure effects inside cells.

Fig. 3.3 is an image of the four-line probe developed by our research group to measure the electronic conductivity of Li-ion cathodes. The four-line probe instrument was milled out of a 15 cm×15 cm copper-clad circuit board (copper sheet bonded to a non-conductive resin substrate). The milled gaps between copper traces were filled with non-conductive epoxy. This was followed by the abrasive removal of excess epoxy with fine-grit sandpaper to produce a flat surface. The copper board electrode leads were connected to the potentiostat (Arbin OptiPlex 380).
The gap between the two inside probes is 10 mm (center to center), while the gap between the inner and outer probes is 0.4 mm. These dimensions were determined by trading off multiple factors. First, it is easier to analyze the experiment if the current is uniformly distributed and one-dimensional in the region between the two inner electrodes. This will be the case if the gap between inner and outer electrodes is sufficiently large relative to the sample thickness, because this region allows the spreading of current injected at the outer electrodes. For typical sample thicknesses (around 100 µm), the gap between the inner and outer probes (400 µm) is sufficient to evenly distribute the current. This was confirmed by computing for a few cases the current distribution using a numerical solution to Laplace’s equation with realistic geometries (sample thickness between 60 and 100 µm). The error
between using Eq. 3.1 and a more detailed numerical calculation to estimate conductivity is completely negligible. On the other hand, if the gap between two probes is too small then particle inhomogeneities (maximum particle size is around 15 µm) can also be a complicating factor. The final consideration for probe geometry is the need to maximize the gap between the inner electrodes to increase the voltage signal within the constraint of the desired sample size.

Each cathode sample was positioned in the center of the copper board (Fig. 3.3) in a symmetric fashion. A circular cork pad was then placed on top of the cover glass, and cylindrical weights were added on top of the cork pad, which helped to evenly distribute the weight. After that, a 0.3 mA current was passed between the two outside probes, and a voltage difference measurement was collected with the two inside probes.

Electronic conductivity was calculated using

\[ \sigma = \frac{L I}{\Delta V S} \] (3.1)

where \( L \) is the length of the sample, \( I \) is the current that passes through the sample, \( \Delta V \) is the voltage between inner lines, and \( S \) represents the cross-section area of the sample. In order to compute 95% confidence intervals for electronic conductivity measurements, the samples were rotated clockwise 90 degrees between each of the five measurements. The error bars in results analysis section are the 95% confidence interval of these five measurements.

Two factors were examined to ensure the accuracy of the four-line probe: probe reliability and cathode stability.

### 3.3.1 Probe Reliability

The four-line probe method was validated by three different duplicative measurements on select samples. First, a square conductive sheet composed of silicone and carbon black (1 mm thick, Cho-seal s6600, Parker Chomerics) was tested by both the four-line probe and
the van der Pauw method, in which needle-like probes were inserted into the four corners [62]. The conductivity of the silicone measured from the new and van der Pauw methods was $365 \pm 10 \text{ mS cm}^{-1}$ and $357 \pm 8 \text{ mS cm}^{-1}$ respectively. Secondly, the conductivity of a cathode sample chosen at random was measured by the four-line probe and by a traditional four-point probe. Because the four-point probe is not able to apply a sustained pressure across the sample, in this comparison a small pressure of 300 Pa was used for the four-line-probe. The resulting conductivities for the four-line and four-point probes were $108 \pm 2 \text{ mS cm}^{-1}$ and $103 \pm 2 \text{ mS cm}^{-1}$ respectively. Lastly, the conductivities determined for the same cathode measured using two different four-line probes with inner gaps of 1 cm and 0.3 cm were $238 \pm 6 \text{ mS cm}^{-1}$ and $236 \pm 8 \text{ mS cm}^{-1}$ respectively. In summary, multiple methods confirmed that the four-line probe produced reliable results for conductivity.

### 3.3.2 Cathode Stability

Multiple considerations were made to confirm that measurements were stable over time. It was found that under constant current, dry electrodes achieved essentially constant voltage after no more than 2 minutes. This steady-state voltage was used in Eq. 3.1 to analyze each electrode. In one case, an electrode was tested over the course of 24 hours and the steady state persisted over that period. For wet measurements (described below), steady state could take as long as 10 minutes to be achieved. Second, the films were moved laterally in two dimensions relative to the probe to allow for observation of cathode variability and to obtain a representative view of the sample. The variation of conductivity was still within 1 standard deviation of the previous measurements for both commercial and laboratory-made films we tested, even though the laboratory-made films have higher variation compared to commercial ones. Third, six cathode films were retested after a month to verify their conductivity stability. This included laboratory-made, commercial calendared, and commercial recalendared films. The resulting measured conductivities were again within error bars of the original measurements.
3.4 Results and Discussion

3.4.1 Electronic Conductivity vs. Porosity

Fig. 3.4 shows the dry electronic conductivity of 4.8 cm$^2$ commercial cathodes across a wide range of porosities. Some cathodes were recalendered to explore the low-porosity range. The electrodes porosities were calculated based on knowledge of their mass, volume and composition, as described in previous work [7]. A clear trend was shown, as the electronic conductivity increased significantly with a decrease in porosity, as expected. However, it is surprising to see the degree of sample-to-sample variation, which far exceeds the measurement uncertainty (error bar) for electrodes of similar porosity, since commercial battery electrodes are expected to have relatively high consistency in manufacturing. For example, cathode samples with around 35% porosity, which is typical of commercial cells, have an average conductivity range from 180 mS cm$^{-1}$ to 280 mS cm$^{-1}$.

In order to describe the relationship between electronic conductivity and porosity on a more quantitative basis, the following empirical equation is used to fit the electronic conductivity vs. porosity behavior.

\[
\sigma = \sigma_0 \frac{1 + (1 - \chi)^{-a}}{(1 - \varepsilon)^{-a} + (1 - \chi)^{-a}} \tag{3.2}
\]

The equation has three parameters: $\sigma_0$ represents the conductivity at zero porosity, which approximates the maximum expected electronic conductivity for electrodes of this composition. This is a useful metric when comparing different electrode compositions. $\chi$ represents the porosity at which $\sigma$ is about half the value of $\sigma_0$, and $a$ is an empirical exponent. Compared to a commonly-used power-law equation for predicting conductivity trends, $\sigma = \sigma_0 (1 - \varepsilon)^a$ [9], Eq. 3.2 better describes the asymptotic trend at low porosity values. The empirical fit with Eq. 3.2 is plotted in Fig. 3.4, where $\sigma_0 = 264 \text{ mS cm}^{-1}$, $\chi = 0.48$ and $a = 8$. 

31
Figure 3.4: Electronic conductivity of dry commercial LiCoO$_2$ films with varied porosity, along with two fitting curves. Error bars indicate the 95% confidence interval of the five measurements made on each sample. $R^2$ for the fit with Eq. 3.2 and Power law was 0.67 and 0.55, respectively.

Decreasing porosity by calendering can be expected to improve electronic conductivity in multiple ways. First, the volume fraction of conductive materials increases. Second, contacts between particles are improved. Third, contacts to the current collector can be improved, though this is not explored in this work (the current collector is removed). Considering the overall electronic resistance of electrodes is a function of particle intrinsic resistance and contact resistance, the trends shown in Fig. 3.4 suggest the particle-contact explanation is the dominant effect. At low porosities, however, the particles are essentially fully connected, and decreasing porosity no longer increases conductivity. The conductivity of most films with a porosity around 35% reaches this upper limit. Lastly, there may be a mechanism that in some instances could cause conductivity to decrease with decreasing porosity. As shown in Fig. 3.5, highly conductive carbon domains are not uniformly distributed and might be reorganized in non-optimal ways during the calendering process.
Figure 3.5: FIB/SEM images of commercial cathode at 45% porosity (a, d), 34% porosity (b, e) and 25% porosity (c, f) at different levels of magnification. The bright gray is LiCoO$_2$, dark grey is carbon and binder (CB) domain, and black is porous region. The nanoporous structure of CB domains is shown in the enlarged images on the right.

Fig. 3.5 compares focused ion beam/scanning electron microscopy (FIB/SEM) images of commercial cathodes with porosities of 45%, 34%, and 25%. These images illustrate the microstructural basis for the results in Fig. 3.4. Image (a) shows larger gaps between particles in contrast to images (b) and (c). Decreased porosity comes mainly from decreasing the size of open pore spaces, though there may be some changes to the carbon domain structure as shown in (d), (e), and (f). The nanopores within parts of the carbon domain are compressed...
more or less depending on compaction from the surrounding active material (LiCoO$_2$) during the calendering process.

3.4.2 Electronic Conductivity vs. Pressure

Cathodes and other battery components are contained under a certain pressure in an assembled cell. Knowledge of how pressure affects electronic conductivity could be beneficial in cell design, and was consequently explored as part of this work. In our experiment, pressure was adjusted by adding different weights on top of the sample cathode. Care was taken to ensure the pressure was distributed evenly across the cathode and substrate.

Fig. 3.6 shows that electronic conductivity is increased modestly by applying pressure to all the cathodes over a wide range of porosities. Laboratory-made and commercial cathodes of similar porosity are marked with the same shape. Both types of cathode films showed the same trends (slope) with compression. In general, electronic conductivity increases with
pressure up to around 6 kPa, and then is roughly constant for higher pressures. Additional data from 10 kPa to 60 kPa was collected (not shown in Fig. 3.6) and confirms this plateau. This suggests that modest external pressure on the cathode could improve its electronic conductivity (from 170 mS cm\(^{-1}\) to 205 mS cm\(^{-1}\) for 36.4% porosity film) by reducing contact resistances, but applying excessive pressure yields no additional benefits in improving electronic conductivity and may even cause safety issues. Overall, electronic conductivity is not a strong function of pressure for the range of values used here. Moreover, one important phenomenon seen with the measured cathodes here is that the conductivity values revert back to what they were before the application of pressure, indicating that the application of modest amounts of pressure doesn’t cause plastic deformation and is a reversible procedure.

3.4.3 Electrolyte Effect

Battery electrodes operate with their pores filled with electrolyte, so understanding and quantifying electronic conductivity in the presence of electrolyte is necessary. For this reason we tested select electrodes under both dry and wet conditions in order to compare changes. A typical Li-ion battery electrolyte is composed of 1 M LiPF\(_6\) in a 1:1 (w:w) mixture of ethylene carbonate (EC) and diethylene carbonate (DEC). LiPF\(_6\) is reactive to H\(_2\)O molecular in the atmosphere; therefore, the experiment needs to carried out in an inert atmosphere such as inside a glove box. On the other hand, it is more convenient to use a salt-free EC/DEC solvent to imitate the effect of the electrolyte interacting with the dry cathode. Experiments using either full electrolyte or just solvent were conducted as shown in Fig. 3.7. In addition, some cathodes were pretreated in vacuum conditions of 34 kPa to allow maximum filling of solvent in porous areas. However, some ethylene carbonate (EC) tends to crystallize under vacuum conditions, so additional cathodes were tested with DEC only. Quantifying the effect of the presence of an electrolyte on cathode materials was achieved with a modified four-line probe procedure. The liquid was applied on multiple spots of each cathode for even solvent distribution.
The presence of electrolyte, depending on experimental conditions, can complicate the measurement of electronic conductivity. Under transient conditions the overall electrode impedance is a complicated function of electronic and ionic conductivity, exchange-current density, and double-layer capacitance [59]. However, ionic conductivity would not be expected to have a large effect on the overall measured conductivity for transient wet experiments, because ionic conductivity is in general much smaller than electronic conductivity for these materials [53, 58]; and in the experiments in which salt was absent, ionic conductivity would be zero. Nevertheless, for our purposes it is important to fully eliminate or decouple these other factors and measure only the electronic conductivity under wet conditions. For this reason voltage data are collected only after the establishment of a steady state (up to 10 minutes after imposition of constant current). Copper contacts, which can be considered blocking electrodes, are used to inject and remove constant current (0.3 mA) under modest voltage differences (0.5 V or less). Therefore, little to no faradaic or double layer current occurs at the external contacts at steady state; likewise the active material cannot be a steady source or sink of ionic current across the sample because the lattice sites needed for the reaction are finite. Under these conditions, only the electronic pathways would be a means of steady current and thus Eq. 3.1 is still valid.

Fig. 3.7 shows the electronic conductivity of Li-ion cathodes in the presence of electrolyte or solvent. Results for the different liquids and procedures were similar. The error bars are not shown because of difficulty in repeating measurements on the wet film, which could be damaged by repeated measurements. Based on the error bars in Fig. 3.4, we estimate the relative uncertainty of the wet conductivities to be 1-3%.

Introducing EC/DEC solvent into cathodes reduces electronic conductivity of those cathodes to 35%–39% of the corresponding dry electronic conductivity. This suggests that the presence of a liquid phase in electrodes is a significant obstacle to electron transport. Also, as shown in Fig. 3.7, the dry conductivity data appear more scattered than do the wet conductivity data, meaning the application of solvent in electrodes reduced the apparent
Figure 3.7: The effect of the presence of solvent on electronic conductivity of commercial LiCoO$_2$ cathodes. *no vac* means no vacuum condition applied, while *vac* means vacuum condition applied to increase wetting of liquid. The lines in part (a) come from fitting to Eq. 3.2. The line in part (b) is a least squares linear fit for the combined results and has slope 0.42 and $R^2 = 0.41$. 
conductivity variation for cathodes of the same porosity. In summary, dry and wet maximum conductivity using our fitting equation gives a $\sigma_0$ value of 234 mS cm$^{-1}$ and 90 mS cm$^{-1}$ respectively, where $\sigma_0$ for wet conductivity is 0.38 times that of dry conductivity.

Our observation that electronic conductivity decreases upon the introduction of liquid in the electrode has been observed previously [9, 63, 64]. Some possible reasons can be offered, including (1) an increase in the dielectric strength of the gaps between particles, (2) swelling of binder, and (3) formation of resistive surface films. All of these explanations rely on the fact that a significant component of the overall electronic resistance in a composite electrode is due to particle-to-particle contacts. Explanation (1) is based on the idea that liquid solvent and electrolyte in the void space between particles increases the dielectric strength of said space, meaning a higher local electric field is required in order to transport or tunnel electrons across the small gaps between solid particles. While we don’t know the dielectric strength of the liquid materials used in this work, values for other organic solvents are typically many times that of air [65, 66], and hence liquids could obstruct current flow. Explanation (2) is based on the observation that PVDF swells in the presence of electrolyte [63, 67]. Such swelling would allow or cause small carbon particles to dislocate, leading to larger gaps and hence resistance between particles. Explanation (3) recognizes that when solvents and electrolytes are combined, corrosion-type reactions could take place—forming a so-called solid-electrolyte inter-phase (SEI) and leading to additional surface resistance on particles. The formation of this surface film is known to be a large source of charge transfer resistance [68]. While the formation of SEIs is normally associated with the initial cycling of an electrode, incipient films could have formed in the case of our experiments.

Which of the above three effects is most significant? As shown in Fig. 3.7, the use of different solvent mixtures and the absence of salt makes only modest difference in the ratio between wet and dry conductivities. This suggests that dielectric strength and film formation (explanations 1 and 3) are less likely to be significant as they would be dependent on liquid composition. Binder swelling is therefore a more likely explanation. At this point we are not
Figure 3.8: Electronic conductivities of laboratory-made baseline cathodes, with those for commercial cathodes as a comparison (see Fig. 3.4, which also contains corresponding confidence intervals). The line is a fit using Eq. 3.2 with $\sigma_0 = 210 \text{ mS cm}^{-1}$, $\chi = 0.45$, and $\alpha = 10$. $R^2$ for the fit is 0.67. Vertical lines show the 95% confidence interval for each laboratory-made sample.

able to perform the same level of microstructure analysis of wet samples as we do for dry samples, in order to fully understand this effect. Further work is needed in this area.

3.4.4 Electronic Conductivity of Laboratory-made Cathodes

The intention of fabricating cathodes in our laboratory is so the composition could be varied. While the exact active material and carbon are changed, the laboratory-made films can nevertheless be compared to the commercial films for the baseline weight fraction of the active material.
In Fig. 3.8, laboratory-made cathodes with the baseline composition show the trend of electronic conductivities with porosity similar to the commercial cathodes. The laboratory-made cathodes have a lower average electronic conductivity than those of commercial cathodes, and also modestly increased variation in conductivity. For instance, electronic conductivity of laboratory-made cathodes and commercial cathodes near 35% porosity is 132 ± 52 mS cm$^{-1}$ and 250 ± 37 mS cm$^{-1}$ respectively, (in this case, ± indicates standard deviation rather than a confidence interval).

We can compare the microstructure of the commercial (Fig. 3.5) and laboratory-made (Fig. 3.10 (a)) cathodes at baseline composition. Most notably, the active material (LiCoO$_2$) particles for the commercial cathodes are 3-4 times larger than those used in laboratory-made cathodes. Other modest differences in the structure and conductivity of the materials used in the respective cathodes could account for the relatively lower effective conductivity of the laboratory-made cathodes. Additionally, the commercial cathodes may have a superior mixing or drying process. While not shown here, we observed occasional larger aggregations (8-10 µm) of active particles in the laboratory-made cathodes. Nevertheless, the balance of evidence suggests that while the laboratory-made films have some fabrication flaws, they are of sufficient quality to draw scientific conclusions with respect to trends in conductivity performance.

### 3.4.5 Carbon and Binder Domain

The carbon volume fraction is one of the main factors controlling the bulk electronic conductivity of cathodes. Quantifying the relationship between electronic conductivity and the amount of carbon additive is crucial to optimal cell design.

Previous work by the Battaglia group has explored the effect on conductivity with changes to carbon-to-binder ratios and carbon-to-active material ratios [55, 57, 63, 69, 70]. The carbon-to-binder ratio used in this work is around 0.7, which is near the suggested optimal ratios for cathode composition when active material loading is at range of 86.5 wt% to
94.5 wt% [57, 69, 70]. However, we slightly increased the binder-to-carbon ratio when we decreased the amount of carbon, as shown in Table 3.1. The extra free binder is likely needed to stabilize the active material and sustain the mechanical stability of the cathode film [69].

Based on imaging studies, at typical compositions most binder is distributed inside discrete nanoporous carbon and binder domains [7, 69], which can be seen as well in Fig. 3.5. Therefore, in this work we chose to keep the carbon-to-binder ratios nearly constant while varying the amount of carbon and binder relative to the active material. Assuming the carbon and binder (CB) domain has a volume fraction $\epsilon$ of nanoporosity, then the total volume fraction of the CB domain within the cathode would be

$$v_{CB} = (v_c + v_b)/(1 - \epsilon), \quad (3.3)$$

where $v_c$ and $v_b$ are respective the volume fractions of carbon and binder solids only, and may be computed using masses and densities. For instance, $v_c = m_C/({\rho}_C \times V_{tot})$, where $m_C$ and $\rho_C$ are the mass and solid density of carbon in the cathode respectively. $V_{tot}$ is the overall volume of the cathode. The $\epsilon$ value used here is 0.5. In a previous work estimating the nanoporosity of the carbon and binder domain mixture, this value was around $0.5 - 0.65$ [7].

The laboratory-made cathodes were made according to the composition in Table 3.1. The amount of NMP solvent needed to be adjusted as the amount of carbon and binder increased in order to maintain desired slurry viscosity for casting. Fig. 3.9 shows that electronic conductivity is greatly increased by increasing the CB domain volume fraction, with data approximately following a power law growth trend. Compared to the carbon mass fraction, the CB domain volume fraction is a more effective metric in predicting electronic conductivity (regardless of porosity) because it accounts for the fact that conductivity is a volumetric phenomenon and dispersion of the more conductive phase will control overall conductivity. Fig. 3.10 shows the microstructure of electrodes of different carbon fractions at 35% porosity. Cathodes with a 2 wt% carbon mass fraction correspond to a 10-20% CB domain volume
Figure 3.9: The effect of changing carbon fraction on electronic conductivity of laboratory-made LiCoO$_2$ cathodes. CB domain volume fraction is estimated as described in the text. The cathode compositions are given in Table 1. Vertical lines show 95% confidence intervals. The fit line is a power law with prefactor 0.9 mS cm$^{-1}$ and exponent 1.7.

fraction, as shown in Fig. 3.10 (a), in which the carbon domain is not likely to be fully percolated, that is to form a continuous path across the entire cathode [7]. Thus, electrons need to transfer repeatedly between carbon domains and the active material in order to cross the electrode. However, cathodes with a 6 wt% carbon mass fraction correspond to a 30-40% volume fraction of the CB domain, shown in Fig. 3.10 (c). In this case the CB domains more or less interface with one another, so they are much more likely percolated in three dimensions. This accounts for the much higher conductivity (Fig. 3.9) as the amount of carbon is increased.
Figure 3.10: FIB/SEM images of (a) 2%, (b) 4%, and (c) 6% carbon weight percentage of cathodes, as specified in Table 3.1 and each at porosity around 35%.
3.5 Conclusion

This chapter used a four-line probe to quantify electronic conductivities for both commercial and laboratory-made LiCoO$_2$ cathodes, and investigated the effect of several important factors on electronic conductivity. Generally, reducing the porosity improved electronic conductivity by enhancing inter-particle connection. Electronic conductivity was greatly increased by raising the carbon domain fraction. Conductivity is less sensitive to the modest application of external pressure. The presence of an electrolyte or solvent reduced electronic conductivity to about 40% of the dry value in our experiments.

Combining this work with previous work measuring the ionic conductivity of Li-ion cathodes [53], we see that the wet electronic conductivity of the baseline commercial cathodes is around 80 times greater than the ionic conductivity for porosity of 35%, which means that ionic conductivity is generally the more limiting transport mechanism for pristine (uncycled) cathodes. Increasing the amount of carbon and binder increases electrode tortuosity, thus decreasing ionic conductivity; therefore, there is no need to increase the fraction of carbon domain in the interest of optimizing transport properties. However, electronic conductivity is more sensitive than ionic conductivity to changes in microstructure and composition. For instance, decreasing carbon fraction by a small amount may cause a rapid decrease in electronic conductivity. So, in practical manufacturing terms, it is safer to over design electronic conductivity to ensure a certain level of performance over the cell’s lifetime.

The results from this work can also be used to refine computer models. For instance, the conductivity parameters used in a Newman-type model must be specified, and property dependence on fabrication parameters is not necessarily known [39, 40, 54]. Thus, Newman-type models can fail to predict overall battery performance when changing the composition of electrodes. This work provides an improved experimental understanding of the connections between fabrication, microstructure and cell performance.
Chapter 4
Imaging

4.1 Introduction

Studying cell performance from a 3D microstructure perspective has become an increasingly valued topic [6, 15, 32, 34, 35, 41, 42, 52, 71, 72]. Conventionally, surface structure is used to characterize and analyze the microstructure, using electron or optical microscopy. Compared to surface structure, a 3D structure can obtain information on features such as particle connectivity and phase tortuosity, both of which play key roles in determining electrode performance [32, 35, 42].

To date, the 3D microstructures of porous electrodes have mostly been obtained using X-ray computed tomography (CT) and focused ion beam/scanning electron microscopy (FIB/SEM) [6, 34, 35, 72, 73]. This chapter first reviews the two tomographies and their applications in the field of batteries, then demonstrates image collection procedures for both tomographies from our study, and lastly shows some the techniques for image processing and 3D image reconstruction.

4.2 Image Tomography

This section demonstrates the working principles of two image tomographies: X-ray CT and FIB/SEM. It then compares the advantages and disadvantages of these two imaging techniques in our study.
4.2.1 X-ray Tomography

X-ray tomography is based on the differential absorption or scattering of an X-ray source by a specimen, thus revealing the internal attributes of the sample’s structure. Fig. 4.1 (a) demonstrates a schematic of X-ray tomography. A cylindrical sample is mounted on a precision positioning stage used for sample centering and rotation, then exposed to parallel and monochromatic synchrotron X-ray radiation at high keV. As the X-rays penetrate the sample, they are partially absorbed by the heavy elements in the electrode. The transmitted X-ray beam is converted into visible light by a scintillator, then generating a radiographic optical image of the sample. The optical image is then magnified by an optical objective, reflected by a mirror, and recorded by a CCD camera. The sample is rotated a total of 180 or 360 degrees, and projection images are recorded at small degree increments during the rotation [74]. Then digital geometry processing is used to invert the data and generate a 3D image of the object from the series of radiographic images.

There are two categories of X-ray tomography: laboratory tomography and synchrotron radiation X-ray tomography. In laboratory tomography, the X-ray beam diverges from a tube source. X-ray tube sources provide relatively low photon fluxes and the spatial resolution varies from a few millimeters down to 1 \( \mu \)m. The typical acquisition time is approximately 15-30 minutes to obtain a 3D volume of \( 1024 \times 1024 \times 1024 \) voxels. In contrast, synchrotron sources bring more photons where the X-ray beam is parallel. The spatial resolution typically varies between 50 nm and 40 \( \mu \)m. The typical acquisition time is on the order of a few minutes to obtain a volume of \( 1024 \times 1024 \times 1024 \) voxels [74, 76]. In summary, synchrotron radiation X-ray tomography is desirable due to a higher photon flux over a broad energy range, enabling large-volume 3D X-ray tomography with nanometer scale resolution. The Argonne National Laboratory has a synchrotron facility which can be accessed for free (only for academic purposes).

Although X-ray nano tomography delivers useful results, the carbon additive in the electrode has poor X-ray absorption [6], meaning the carbon additive is often not shown in the
resulting image. The contrast in the image between carbon and pore regions is invisible. Essentially, X-ray tomography distinguishes microstructural features which have significant differences in their X-ray absorption qualities. Furthermore, synchrotron resources are limited, making routine measurement difficult.

### 4.2.2 FIB/SEM

Fig. 4.1 (b) shows a schematic of the FIB/SEM tomography process [77]. The sample is tilted 52 degrees in such way that the Ga ion beam is perpendicular to the sample surface. Thin sections from the exposed electrode surface are milled by Ga ions and imaged by SEM. A
series of images is acquired by repeating this process. The ion beam is moved with resolution up to 10 nm step by step relative to a reference mark milled on the sample. The ion beam pauses after each milling to allow for the capture of a SEM image; shown by the $e^-$-vector in Fig. 4.1 (b).

In comparison to X-ray tomography, FIB tomography currently occupies a niche defined by its resolution. It is widely used in the semiconductor and material science industries to detect flaws on nanometer scale [78]. The typical resolutions that can be reached are in the range of tens of nm down to 5 nm [78]. The FIB/SEM approach is used to characterize nanometer-sized LiFePO$_4$ (LFP) electrodes and micrometer-sized LiCoO$_2$(LCO) particles with great detail (e.g. cracks in particle) [35, 79]. However, FIB/SEM techniques are limited in the sample volume that can be analyzed [6, 78].

4.2.3 Application

Which tomography is more applicable for porous battery electrodes? There are two main factors to consider: tomography resolution and volume of the sample that can be analyzed. Regarding sample size, in order to adequately represent the electrode microstructure, the characterized volume of the electrode should be equivalent to a cube having a minimum length of 7.5 times the particle diameter [32, 41, 80]. Thus, it is crucial to balance the resolution and sample volume while choosing a suitable tomography method. Fig. 4.2 compares the range of sample volumes and resolutions between various tomography techniques. As shown, X-ray tomography and FIB tomography cover sample volumes from 1 cubic micrometer to 10 cubic millimeters. However, there is a trade off between the analyzed material’s volume and the voxel resolution. The bigger the volume of the sample, the bigger the voxel size.
Figure 4.2: Tomography scale mapping with a focus on comparing X-ray tomography and FIB tomography (adapt from Ref.[78]).

The Li-ion battery has an average particle size of 0.2 micrometer (LiFePO$_4$) to 10 micrometers (LiCoO$_2$), depending on the active material [8, 81–83]. It is evident that FIB tomography is more appropriate for LiFePO$_4$ electrodes in Li-ion batteries because of its high resolution at the sub-micron and nanometer range. Based on the 7.5-particle-diameter rule of thumb, the estimated minimum representative volume size for LiFePO$_4$ electrodes is around 8×8×8 μm, which is at the center of the FIB/SEM practical range, according to Fig. 4.2. LiCoO$_2$ active material has a relatively narrow particle size distribution (5-15 μm). The minimum representative size would be around 80×80×80 μm, which is at the upper edge of FIB/SEM’s sampling capacity.

In contrast, alkaline batteries have a larger particle size distribution, ranging from sub-micrometer to 50 micrometers for the active material (EMD). Therefore, it increases the complexity of choosing a satisfactory tomography tool. According to the 7.5-particle-diameter rule of thumb, a minimum volume of about 225×225×225 μm would be required for a
representative 3D structure, assuming median particle size is about 30 µm. Thus, X-ray tomography is more suited to acquiring a sample size this large; however, the lab X-ray tomography may not resolve the nanoscale features of alkaline batteries (nanoscale features of alkaline batteries are explained further in section 2.2.1). On the other hand, FIB/SEM can resolve nanoscale features yet has a sample size limitation. Hence, a better solution combines X-ray tomography and FIB/SEM, taking advantage of each method.

4.3 Acquiring Image Series

This section outlines the steps of acquiring a series of images using FIB/SEM, including sample preparation and FIB/SEM operation.

Sample preparation for a series of FIB/SEM images depends on battery electrode size and composition. Li-ion battery cathodes are thin (∼100 µm) and include a binder to hold the particles in place. Unlike Li-ion batteries, alkaline battery cathodes are in the form of an annular pellet (millimeter size) and are contained in a metal can under a considerable amount of pressure. A graphite additive acts as a lubricant, binder, and electronic conductivity promoter. There is no additional binder to hold the particles in place after the pellets are formed. Thus, we need to prepare the samples differently for each battery type to best imitate their electrodes structure. The common preparation steps are as follows:

(a) Fabricate the electrodes. For Li-ion batteries, the electrode is fabricated in the manner described in Appendix A, which is similar to how commercial batteries are made. For alkaline batteries, even though commercial cathodes are a hollow cylinder, for our research, regular cylindrical pellets were used to simplify fabrication and testing. According to Fractal Structure Theory, using this differently shaped cathode has no effect on microstructure [85, 86]. The alkaline pellet cathodes are fabricated by first adding the cathode mixture (discussed in Sec. 5.3.1) into a 20 mm diameter cylindrical, hardened steel, dry pressing die set (Across
Figure 4.3: Preparation steps for FIB/SEM series of imaging: (a) fabricate alkaline battery cathode pellet, (b) mount the electrode on the stub, (c) mill a trench in the middle of sample, (d) adjust the eucentric height. Image adapted from Ref. [84].

International) (see Fig. 4.3(a)), then pressing the die with use of a hydraulic press (model 3912 by Carver).

(b) Mount the electrodes onto a stub. The stub shown in Fig. 4.3 (b) is used to take the sample in and out of the FIB/SEM chamber (FEI Helios Nanolab 600) and is screwed tightly onto the stage, which allows the instrument to move the sample position by moving the stage. Electrodes are mounted on top of the stub with double-sided carbon conductive adhesive tape (Agar Scientific). This tape can secure light weight electrodes (such as Li-ion battery electrodes), but sometimes cannot adequately secure thicker (millimeter scale)
alkaline battery electrode pellets to resist drift when the sample is tilted. To secure these larger samples, tape may be applied to the sides or even the top of the sample, so long as the area of interest is not obstructed. Mounting the sample properly on the stub is a small yet critical step for a high quality series of images. Small sample drift can cause serious misalignment of the image series on the microscale.

(c) Deposit a conductive layer on the electrode surface. The conductive deposit (also referred to as a coating) generally serves two purposes: to reduce charging for a non-conductive sample or semi-conductive sample and to smooth the surface edge effect. Charging is produced by a build-up of electrons in the sample and their uncontrolled discharge, which can produce unwanted image artifacts, such as washed out areas or other distorted features. Edge effects are caused by the increased emission of electrons from edges and peaks within the specimen, which causes a poor image signal in the vicinity. Gold/platinum (Au/Pt) sputter coating (around 5 µm) is applied beforehand in the BYU microscopy lab.

(d) Adjust the sample to eucentric height. As shown in Fig. 4.3 (d), eucentric height is the height at which both the ion beam and electron beam are focused on the same point. Thus, the sample image does not shift even as the sample is tilted. For details about how to adjust the sample to eucentric height, see the Helios operation tutorial in Appendix B.

(e) Prepare the area around the sample. Preparation and cleaning procedures differ depending on the sample location. If obtaining 3D images from the middle of the sample, milling a trench, as shown in Fig. 4.3 (c), is necessary to allow an unobstructed view of a cross section of the sample interior. Generally, the length (Y) of the trench should be twice its depth to enable the image plane to reflect the electron beam signal. Otherwise, the surface of the sample will obstruct the lower part of the cross section. Alternatively, we can collect a series of images from the edge area. This only requires eliminating edge irregularities. Considering the large sample size we need for alkaline batteries, taking an edge sample significantly reduces milling time. However, the particles from the edge tend to settle or even collapse during the milling process due to pressure release or imbalance. This can
be improved through choosing sample sites that have smooth and solid edges before milling is started.

After the above sample preparation steps are complete, the electrode is ready for imaging. We collected our images using software called *Slice and View* which comes pre-installed with Helios. *Slice and View* is software that controls milling and imaging to according user specifications. *Slice and View* first mills a fiduciary mark shown in the upper right hand corner of Fig. 4.4. The ion beam moves along the Z direction step by step relative to the fiduciary mark. The ion beam pauses after it finishes each slice and the e-beam automatically takes an image. It takes up to 36 hours to acquire an image stack of 130 images at half micron intervals. Each image has a resolution of 4096×3536 pixels. Additional details are found in Appendix B.

Figure 4.4: Acquiring a series of FIB/SEM images using Slice and View. The ion beam moves along the Z direction step by step relative to the fiduciary mark at the right corner.
4.4 Image Pre-processing

There are a few steps to pre-process a FIB/SEM image before analysis, including image stretching, aligning, cropping, and correcting image defects (e.g., noise reduction with filters). Image stretching and alignment work was collaborated with the porous media group in IMTEK at the University of Freiburg.

4.4.1 Image Alignment

The acquisition of the image series can last for 30 hours or more, so drift in all three directions can become significant [87]. The resulting errors become obvious when stacking images into a 3D structure [80].

During serial milling, the ion beam moves with high precision at a constant specified step size in the Z direction according to the fiduciary mark, as seen in Figs. 4.4. Therefore, the working distance between the e-beam and the image plane (XY) increases as the ion beam moves in the Z direction, as illustrated in Fig. 4.5. This causes the focus in the XY plane to shift. Though the e-beam is self-adjusting to compensate for shifting, the XY plane is being cut at an oblique angle to the e-beam (see Fig. 4.5) and the self adjusting alignment is not perfect.

In this work, all images in the stack are aligned with Matlab code. The image stack is aligned with respect to a single arbitrarily chosen unmilled area, which shows up throughout the image stack. The computer code for alignment is included in Appendix C.1. In some cases, a desktop computer may not be able to handle the huge data sets. Alignment in a supercomputer is optional.

4.4.2 Image Stretching

In addition to drift compensation, further correction procedures are needed because of the geometrical peculiarities in dual beam systems. The oblique imaging angle (52 degrees) leads
to a distortion in the \( y \) direction that has to be corrected. As shown in Fig. 4.5, the e-beam observes the sample size is \( dy' \), which is shorter than the original image \( dy \). The relationship between these two can be described as

\[
dy = \frac{dy'}{\sin(A)}
\]  

\( A \) is 52 degrees. Therefore, the height of the electrode is 1.27 times that of an image in FIB/SEM. Figs. 4.6(b) is the stretched image of original FIB/SEM image (a).

4.4.3 Image Cropping

As shown in Fig. 4.6 (b), the FIB/SEM image contains extra areas which are not used for statistical analysis. Therefore, cropping is a prerequisite to 3D reconstruction [32]. Depending on image size, cropping a set of images can be done using the ImageJ software. This
Figure 4.6: (a) Original FIB/SEM image, (b) stretched FIB/SEM image, (c) cropped FIB/SEM image.

Involves the following steps: importing the image sequences, cropping the images, and exporting all the images in sequence. If the image size exceeds the allowed size in ImageJ, an alternative solution is to crop the image using Matlab. Most Li-ion image sets in this work were processed using ImageJ. The alkaline image set was cropped by a Matlab routine in which the coordinates of the final image were specified in advance.

4.4.4 Correction of Image Defects

Ideal images are clear (no extraneous features), have high signal fidelity (uniform response) and high contrast (to differentiate different materials). Common problems with real images include both a curtaining effect and an image signal that fades as you move through the stack of images. They can also be grainy, and some objects from deeper layers show up in the topmost layer due to pores. These defects diminish the ability of a computer to distinguish between objects.
The curtaining effects occur because of differences in ion milling speed due to material morphology and solidity, causing curtains to occur at the interface of two materials. Curtaining appears as vertical stripes in Fig. 4.7 (a). In our case, there are three phases with different hardnesses: the active material, carbon additive and pore, making the curtaining effect challenging to avoid. However, there are a few approaches that can reduce the curtaining effect. First, applying a thick layer of the Au/Pt coating on top of the sample is quite effective to help reduce curtaining in the top 10 microns of the image, and is used in this work. Second, filling the pore area with a solid (such as a polymer), so the ions hit the filling material instead of the pore region (which causes more ion divergence leading to curtains) has been shown to reduce this effect [35, 88]. Another benefit of filling up the pores is that the objects in deeper layers won’t show up in the front layer. However, we did not use the filling method in this work because it generally obscures the presence and morphology of carbon domains and conflates them with the surrounding pores [89].

Another way to correct for curtaining is through image processing, which suppresses information that is irrelevant to specific image analysis. Filter tools are good for avoiding irrelevant image information. For instance, a median filter outputs the median value of the specified matrix around the corresponding input pixel. This can reduce curtaining and graininess, as shown in Fig. 4.7 (b).

In general, when collecting a series of images with different depth, images appear darker and more grainy in the final collected images than in the first collected images. Our target average luminosity was 0.4, and we therefore adjusted the brightness of each image by calculating the mean pixel value of each image and then multiplying by a factor so that each picture has the same luminosity of 0.4.
Image segmentation is the process of partitioning a digital image into multiple segments. The goal of segmentation is to simplify or change the representation of an image into something that is easier to analyze. Segmentation accuracy determines the success or failure of structural analysis. The complexity of segmentation increases with the number of phases to be identified. Battery electrodes often involve three phases, which is more challenging to segment than a binary system.

Image segmenting was attempted using three different methods: manual segmenting, computer segmenting, and human assisted computer segmenting. In the end, we showed that a hybrid method combining computer segmentation and manual segmentation provides the highest efficiency while maintaining a satisfactory level of accuracy. Danilo Bustamante and William Lange in BYU’s Electrical and Computer Science Engineering Department provided assistance developing the computer segmenting algorithms.
4.5.1 Manual Segmentation

Manual segmentation is necessary as a benchmark and validation for any other type of segmentation. Manual segmentation classifies each pixel carefully with a human eye, providing the highest quality of our three segmentation methods. However, it takes about 10 hours in Photoshop to segment an image with dimensions of $100\times120 \, \mu m$ (pixel size of 52 nm). Fig. 4.8 shows an example of careful manual segmentation on an alkaline battery electrode. Using human recognition of image content, this segmentation method is capable of categorizing each individual pixel, especially in the region marked with red, where an object from a deeper layer shows through in the front layer. The human brain can identify the object through referring to surrounding information. Also, because the texture of the active material is a nanoporous structure (marked with blue boxes), it is tedious to segment. We simplify these structures as branch structures.

![Figure 4.8: Manual segmentation: (a) The original FIB/SEM image, (b) the image after manual segmentation. Blue box(1) shows the nanoporous region in EMD. Red box (2) shows an inside object showing up in the top layer. Gray is active material, black is carbon additive and white is pore.](image-url)
4.5.2 Computer Segmentation

Computer segmenting uses computer algorithms to differentiate pixels. Recognition of discrete objects (i.e., individual particles) in FIB/SEM images remains a challenge [32, 78, 90]. Commonly used computer algorithms for segmenting FIB/SEM electrode images include threshold and filter-related tools, such as the mean algorithm and median filter [32, 42, 90]. Unfortunately the processing of each material type and each detection mode require specific treatment and therefore, no standard computer segmenting procedures for quantification can be proposed.

Fig. 4.9 shows the main steps for computer segmentation in Matlab, using an image from the middle of the 3D image set as an example. Computer segmenting is executed in Matlab as follows: (a) Balance and smooth the image using mean and median filter tools. (b) Emphasize the most obvious edges using rangefilt, then use these edges as boundaries for growing regions (explained in step (e)). The rangefilt algorithm outputs pixels with the range value (maximum value minus minimum value) of the 3-by-3 neighborhood around the corresponding input pixel. (c) Identify inter-pore regions by analyzing the mean of the entropy-filtered image, looking for pores above a minimum size (0.5 µm). (d) Mark the centers of these pores as seeds (white dots), and grow the pore regions starting from the seeds until the boundaries from step (b) are reached. (e) Separate the carbon and pore regions by evaluating the correlation of pixels in the X and Y directions. Both carbon and pore region pixels have similar means and standard deviations; however, the curtaining effect only shows up in the solid material, not in pore regions. Thus, carbon has a different pixel correlation. (f) Distinguish active material regions by calculating the means and standard deviations of pixel values. Usually, the active material has a higher mean pixel value and a lower standard deviation than the carbon and pore regions.
Figure 4.9: Computer auto-segmenting for 76 × 173 μm alkaline cathode: (a) pretreated image, (b) rangefilt image, (c) entropy filtered image, (d) seeds for the pore regions, (e) image exhibiting curtaining effect, (f) segmented image. In the final segmented image, white is pore, black is carbon, and gray is EMD.
To sum up, the main principle for computer segmentation is using pixel mean values to distinguish active material from carbon and pore domains, because the active material has a higher mean pixel value. One can then use pixel correlations between the X and Y directions to distinguish carbon and pore regions since the curtaining effect shows up in carbon, not pore regions, resulting in an asymmetric correlation in the X and Y directions for the carbon phase. Finally, the pore region grows until it hits a boundary explained in the steps above.

The drawback of computer segmentation is that the algorithm threshold value is specified for certain images, meaning that one set of well-adjusted threshold values for one image may still work well with closely neighboring images, but the set of threshold values cannot be applied to a large set of images. Fig. 4.10, column 2 applies the computer segmentation code used for Fig. 4.9 to the the first and last images of the set, corresponding to (a) and (b) below. The carbon phases are mistaken as pore phases.

### 4.5.3 Human-assisted Computer Segmentation

To avoid adjusting the threshold value for each image, a technique we refer to as human-assisted computer segmenting is attempted to intelligently adjust the thresholds for the image series. Human-assisted computer segmenting integrates human phase recognition into the computer segmentation process. At certain pre-defined intervals, human input is required to establish individual phase features, which is done by selecting three regions for each phase. A guideline for choosing each of the three regions is to select regions that are a diverse representation of that phase within the whole image. Upon human recognition of a specific feature of each domain, the computer compares groups of pixels to the selected features, then determines the pixel group’s identity, as shown in Fig. 4.10, column 3. This is also called “machine learning”.

Because of the similarities between carbon and pore regions, human assisted computer segmenting tends to identify small pores as carbon. In the end, to ensure accurate segmentation above 0.5 micrometers, all images are first segmented by computer into only two phases.
<table>
<thead>
<tr>
<th>Raw</th>
<th>Computer segmentation</th>
<th>Human-assisted computer segmentation</th>
<th>Hybrid computer segmentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Image 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Image 2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.10: Matrix of different image segmenting techniques for the first and last images (76 x 173 µm alkaline cathode) of the image set.
Figure 4.11: (a) Manual segmented FIB/SEM image in Fig. 4.8, (b) FIB/SEM image in Fig. 4.8 was segmented using hybrid computer segmentation method, (c) volume fraction comparison between hybrid computer segmenting (b) and detailed manual segmenting (a) to validate hybrid computer segmentation method.
(active material and pore), then the carbon phase is marked manually using photo editing software, since the carbon domains are quite large and continuous compared to the small and dispersed pore regions. This method has been found to be the fastest way to segment all the images. We have named this method *hybrid computer segmenting*. It only takes 2-3 minutes per image to mark the carbon phase in Photoshop using the paint bucket tool (resulting segmented image shown in Fig. 4.10, column 4)

Figure. 4.11 compares the results of manual and hybrid computer segmenting. Hybrid computer segmenting (b) only catches features larger than 0.5 µm, so it only shows inter-pores. In contrast, manual segmenting (a) captures features above 100 nm. As a result, the volume fraction of carbon is comparable between manual and hybrid computer segmenting since carbon is bigger than 0.5 µm (c). However, the pore volume determined by hybrid computer segmentation is much less than that determined by manual segmentation, because nanopores ranging from 100 to 500 nm in size are identified as EMD during computer segmentation. Based on the volume comparison (c), an estimated 7% of EMD’s volume fraction are pores ranging in size from 100 to 500 nm.

### 4.5.4 Advanced Imaging Techniques

Another concept to make segmentation easier is obtaining multiple images of the same slice under different microscopy conditions. By modifying these conditions before images are taken, each image will carry different information about the same objects. Multiple images also can provide information that single image could not. A computer can analyze the images separately and then combine them into one image to accurately identify all three phases.

This section demonstrates a few ways to manipulate instruments in order to increase the contrast between the three phases. Some exploratory image segmenting work was done using multiple images in this section. This exploratory work made image segmentation easier (results are not shown here). We did not apply this new technique to the 3D structures in
this work because the 2D images for 3D reconstruction were already segmented before the new technique was developed.

Figure 4.12: Images of Li-ion battery (Toda 523, particle size around 10 micrometers) taken under various operating parameters, (a) 5kv, SE mode, ETD; (b) 5kv, SE mode, TLD; (c) 30kv, SE mode, ETD; (d) 30kv, BSE mode, ETD.

There are two detectors in the Helios instrument, namely, the Everhart Thornley detector (ETD) and the through-the-lens Detector (TLD). These two detectors are mounted at different locations in the chamber: the ETD is located in one corner of the chamber, while the TLD is located inside the electron beam source column. Therefore, the resulting images taken by the two detectors naturally present sample tomography differently because
the detectors respond differently to the reflected signal due to the angle. Each detector has
different settings, such as secondary electron (SE) and backscatter electron (BSE) modes.
In a BSE image, the lighter elements are likely to be washed out because of BSE’s high pen-
etration depth (100 nm), while the SE image captures more of the front layer so the lighter
elements are more visible because SE’s short penetration depth. Increasing the voltage also
enhances electron beam sample penetration by a few nanometers.

Fig. 4.12 shows Li-ion battery cathode images taken with different detectors and under
different voltages and mode settings. This was for a cathode with the following conditions:
90 wt% Toda 523 active material, 5 wt% Denka carbon, 5 wt% Solvey 5130 PVDF binder,
30% porosity. Parts (a) and (b) were taken with the ETD and TLD detectors, respectively.
The luminosity for image (b) is more evenly distributed compared to that of (a) because the
TLD is directly above the sample, and the ETD is located at a large angle relative to the
source e-beam. Images (c) and (d) were also taken with the ETD detector. The top left
corner is noticeably brighter than the bottom right corner in those images because of the
angles of both the ETD detector and the source ebeam. Also, the TLD image (b) highlights
the boundary between carbon and pore regions.

Because acceleration voltage (5 kv to 30 kv) increases from image (a) to image (c), the
carbon region of image (c) is blurred because of increasing penetration depth and presents a
different texture. This allows a computer to distinguish between phases in a different way.
Activating back scatter mode (d) leads to an even higher sample penetration depth, so the
lighter elements such as the carbon domain are almost invisible. Therefore, we can identify
the active material phase easily using this image.

Fig. 4.13 shows images with customized parameter settings for electrodes with small
particle sizes (92 wt% Toda 5050 active material, 4 wt% Timcal C45, 4 wt% Solvey 5130
PVDF binder, 36.1% porosity). Both ETD and TLD allow for custom mode settings. For
example, we can vary suction tube voltage (-245 V to 245 V) and mirror (-50 degree to 50
degree) for the TLD. When suction tube voltage (STV) is positive, low energy secondary
Figure 4.13: Images of Li-ion battery (Toda 5050, particle size around 0.5 micrometer) taken in customized Helios setting. (a) ETD, SE mode, and 5 kV; (b) ETD, SE mode, and 30 kV; (c) TLD, custom mode (245 V STV and -14.1 mirror), and 5 kV; (d) TLD, custom mode (245 V STV and 0 mirror), and 5 kV.

electrons are collected by the TLD detector. But if the STV is negative, low energy secondary electrons are repelled from the TLD detector and only backscattered electrons are detected. The default suction tube voltage and mirror settings (explained below) for the SE and BSE modes are (70 V, -15 degrees) and (-150 V, 0 degrees), respectively. The mirror slider deflects the acceleration path of the SE’s into the detector. Thus, the resulting images appear as though they were taken from different angles.
The characterized particle size of the sample is around 0.5\,\mu m, so high-voltage or BSE modes are likely to blur all particle edges due to the high penetration of small particles shown in (b). Thus, the low-voltage and SE modes (positive STV) are preferred for small-particle-size imaging. Images (c) and (d) are taken with a positive STV and low source voltage. The pore regions of image (c) appear very dark because more secondary electrons are collected by the TLD when the STV is increased. Image (d) presents an even better contrast between material and pores compared to image (d) by adjusting the mirror angle.

In summary, we demonstrated a few ways to manipulate instrument parameters to take images which allow a computer to more easily identify phases for different electrodes. This reduced the difficulty experienced in image segmenting. This potential technique will be continued by another colleague in our group.

4.6 3D FIB/SEM Reconstruction

Reconstructions are an important step in analyzing the statistics of local state distributions in the internal structure of heterogeneous material systems and in estimating their effective properties using deterministic models. This section first explains a key step (coarse-graining) before 3D reconstruction, and then shows how to combine the 2D images into a 3D structure. Finally, we discuss 3D structure visualization techniques.

4.6.1 Coarse-grained Image

For our image set, each image of an alkaline battery cathode is 76.5\,\mu m\times 173.5\,\mu m (xy directions), and there are 130 images in the set (z direction). The xy pixel size is 62.5\,nm, and the step parameter along the z direction is 500\,nm. If we reconstruct these 2D images into a 3D volume without correcting the resolution difference, the 3D matrix will be 1224\times 2776\times 130. Assuming 16\,bytes per voxel, the 3D matrix requires a large amount of computer RAM for effective conductivity computation. It is not realistic to compute conductivity at all length
scales. Also the resulting 3D microstructure voxels (volumetric pixels) will be non-cubic, which is not convenient for simulation.

There are two ways to obtain a 3D microstructure with cubic voxels. The first method is to reduce the step size to 62.5 nm along the Z direction, leading to an extremely long image acquisition time (approximately 15 minutes for each image) for a reasonable sample size. It is not optimal to extend the image acquisition time since it took 36 hours to acquire the current image set. Moreover, since the resulting 3D image has dimensions of \(1224 \times 2776 \times 1040\) (voxel volume); this will exponentially increase computing costs.

The second method is to reduce the resolution of the XY plane to 500 nm, so the 3D volume is 8 times smaller in each dimension than that of the previous option. This will largely decrease computing costs without sacrificing the image accuracy of the structural representation. If the node resolution is above the average size of the smallest phase (0.5 \(\mu\)m), the resulting image can not resolve the smallest phase. In this work, the cutoff node size length scale is 0.5 \(\mu\)m. The features below 0.5 \(\mu\)m are treated as a homogenized property reflected in the intrinsic property \(K_{in}\) of EMD and the carbon domain.

Reducing the resolution of the XY plane is done by coarse-graining the image. Coarse-graining is a technique in which a structure is simplified over a particular volume by using representative averaged parameters. Coarse-graining is done by grouping pixels together and assigning to each group a single domain identity based on the random selection of one of the underlying pixels. Some other methods, such as same voxel and majority win, are also used for coarse-graining [91]. The same voxel method uses the identity of voxels at certain specified positions in the coarse-grain box as the box identity. This method, like the random method used in this work, conserves image statistics. The majority win method adopts the majority-voxel’s identity of the coarse-grain box as its box identity. The majority win method will bias the image statistics but could reduce sample noise.

Fig. 4.14 shows the example image before (a) and after (b) coarse graining. Part (c) compares the volume fraction of the original segmented image with a pixel size of 62.5 nm
Figure 4.14: Coarse graining of a sample image: (a) hand segmented image (Handseg_orig, node size 62.5 nm), (b) coarse grained (CG) image of hand segmented image (node size 0.5 µm), (c) volume fraction comparison between the original image and the coarse grained image.
4.6.2 3D Structure Reconstruction

After the images are coarse-grained, they are ready for 3D reconstruction. The common method for 3D FIB/SEM reconstruction is to stack the 2D SEM images in 3D space and align the pixels of the images in the slicing direction [5, 32, 88, 92]. Some researchers have utilized the *Amira* and *Dirshti* software to reconstruct 3D images in a similar fashion [36, 93]. Our image sets are stacked in *Image J* in the manner shown in Fig. 4.15.
Figure 4.16: 3D visualization of alkaline battery cathode 5 wt% BNB90 at overall porosity of 24% (153 × 347 × 130 voxels, with node size of 0.5 µm), green is EMD, red is graphite and blue represents pore: (a) threshold parameters settings for individual phase visualization, (b) surface view of 3D image; (c) Orthogonal view of 3D image, (d) 3D network of inter-pore structure, (e) 3D network of carbon structure, (f) 3D network of inter-pore and carbon structures.
4.6.3 3D Structure Visualization

The microstructure and the connectivity of the pore and carbon domains are important in describing the flow of ions and electrons in the cathode. The 3D structure visualization in this work was carried out with Image J, by importing the image sequence under the file menu and using the 3D viewer to obtain surface and orthogonal views of the stacked 3D structures. Fig. 4.16 (a) shows how the color threshold was adjusted under the image menu to obtain the individual phase networks. The remainder of Fig. 4.16 presents the 3D alkaline battery cathodes reconstructed with Image J. Parts (b) and (c) are surface and orthogonal views of the 3D structure, respectively. Parts (d) and (e) show the 3D connectivity of the pore (above 0.5 µm) and carbon networks. Part (f) shows the 3D network of carbon and pore space.

4.7 X-ray Tomography

The relatively small 3D FIB/SEM structures we were able to collect may not be adequate for quantitative structure analysis. As we discussed in Sec. 4.2, according to the 7.5-particle-diameter rule of thumb, a minimum volume of about $225 \times 225 \times 225 \, \mu m$ would be required for a representative 3D structure, assuming median particle size is about 30 µm. In order to compensate for this low amount of sampling, lab X-ray tomography was also attempted, to generate a three-dimensional structure of the pellet. X-ray tomography was carried out near the end of this project, and only limited analysis could be performed. A brief summary of the complicated process of obtaining 3D X-ray tomographic structures is given below, including X-ray tomography image collection and 3D computational reconstruction.

4.7.1 Image Collection

Data acquisition was carried out in a facility at the University of Utah using cone beam X-ray micro-tomography (XMT) with a resolution up to 1.85 µm [94]. The sample (about 2 mm$^3$) did not require special preparation and was packed inside a plastic sample tube. The
plastic tube containing the pellet was placed between the X-ray source and the detector. The sample was rotated by 0.36 degrees for each of 1000 steps and photons were passed through the sample. Its projection was collected by a detector. For a given projection, the number of photons detected depends on the density of the sample and the atomic number of the constituent elements. The higher the density and the higher the atomic number, the lower the number of photons passing through the sample. A resulting 2D X-ray projection image is a matrix of attenuation coefficients, which are defined as the ratio of photons counted between the detector and the initial number of photons generated by the X-ray source [75, 94, 95].

4.7.2 3D Reconstruction of X-ray Tomography Images

Once acquisition of projections at different angles is complete, three-dimensional reconstruction is accomplished using a computational reconstruction algorithm built into the X-ray tomography computer, which results in a 3D matrix in which each voxel is characterized by the attenuation coefficient of the material out of which it is composed. Then the reconstructed 3D attenuation coefficient matrix values are transformed into image intensities (gray-scale values between 0 and 255) using a simple linear transformation [33, 75, 96]. Fig. 4.17 (a) shows a reconstructed cathode containing 512 x 512 x 912 voxels (voxel resolution 1.85 μm), and (b) shows a 3D reconstructed image set with a portion of the volume removed.

It is extremely challenging to unambiguously identify each phase from Fig. 4.17. Therefore, segmentation of the images is yet another obstacle in the way of further quantitative analysis. The captured 3D structure in Fig. 4.17 does not allow us to completely distinguish between particles; it is especially difficult to distinguish between the graphite and pore regions [6]. Some advanced computer techniques such as 3D watershed segmentation and finite mixture distribution (FMD) are commonly used with X-ray tomography to classify the composition of each voxel. The details of the X-ray image data processing are outside of the scope of this project and further details can be found elsewhere [71, 75, 95–97].
Figure 4.17: (a) 3D X-ray structure (around $1 \times 1 \times 1.5$ mm) of alkaline battery cathode 5 wt% BNB90 at overall porosity of 24%. The volume contains $512 \times 512 \times 860$ voxels of edge length 1.85 µm, (b) same 3D X-ray structure with a portion of the volume removed.

In this work, the X-ray structure was segmented in two ways. First, the X-ray structure was segmented only into two phases, EMD and carbon/pore. The carbon and pore domains were combined because the small difference in X-ray absorption between carbon additives and pore impedes their discrimination in our X-ray tomographic data. We attempted to use our active material knowledge from X-ray structure to work with the 3D FIB/SEM data. Fig. 4.18 (a) is a cross-sectioned image from the 3D X-ray tomography reconstruction of an alkaline battery cathode. The EMD phase is shown as brighter gray. Part (b) shows the X-ray gray value of individual voxels along the line shown in part (a). Part (b) indicates that a peak with a higher gray value (above 100) is associated with the EMD phase.

If we use the gray value 100 as the threshold to segment EMD from carbon and pore, the volume fraction of EMD in the 3D X-ray structure is 68%, which is underestimaged compared to results obtained from FIB/SEM structures (discussed in Chap. 5). This is likely due to the fact that the X-ray only identified large, solid EMD ($\geq 10$ µm) particles well, while the small EMD particles were mistaken for carbon or pore domains, as shown in Fig. 4.18 (c).

Fig. 4.19 shows the probability distribution and cumulative probability of voxel gray values in the 3D X-ray structure. Part (a) is a continuous bell curve for voxel value distribution, where the threshold for three domains is not distinct. Thus, the image segmentation of the
Figure 4.18: (a) Cross-sectioned image from 3D X-ray tomography reconstruction of 5 wt% BNB90 cathode, (b) X-ray gray value of individual voxels along the line shown in the reconstructed X-ray tomography image, (c) Segmented image of (a) using the threshold value 100. The red color is the combination of carbon and pore domains.
Figure 4.19: (a) Probability of voxel gray value of 3D X-ray structure in Fig. 4.17, (b) cumulative probability of voxel 3D X-ray structure in Fig. 4.17.

X-ray structure even between EMD and carbon/pore is likely arbitrary. Part (b) is the cumulative probability and can suggest the volume fraction of EMD based on the threshold value chosen for segmented X-ray structure data.

Another way the X-ray structure was segmented (discussed in Chap. 5), using the volume fraction obtained from the FIB/SEM structure to determine the voxel gray value thresholds for the three domains.

4.8 Conclusion

This chapter discussed two image tomography methods that can be used to obtain 3D porous cathode structures. The two imaging methods are FIB/SEM and X-ray tomography. FIB/SEM is observed to be more suitable for the Li-ion battery systems we tested because it satisfies both the resolution and sampling size requirements. At the same time, a combination of FIB/SEM and X-ray tomography is superior for obtaining images of alkaline battery cathodes due to the large particle size distributions of this battery type. Additionally, FIB/SEM has the advantage of detecting carbon additives, while X-ray tomography displays extremely low contrast between carbon and pore domains; therefore, the spatial
distribution of carbon additives cannot be reliably identified. Thus, FIB/SEM is the main
tomography tool employed in this study.

Protocols and techniques for acquiring, processing and segmenting series of FIB/SEM
images were developed as part of this work. These images are generally larger than typi-
cal 3D FIB/SEM structures obtained in other reported studies and represent a substantial
amount of work. Many image segmenting methods were attempted, namely manual seg-
mentation, computer auto segmentation, human-assisted computer segmentation and hybrid
segmentation. The best solution to segment a series of images for alkaline cathodes is hybrid
segmentation, which is done by using a computer algorithm to segment the image into active
material and pore phases, then identifying carbon phases manually. Some other advanced
image-acquiring techniques are under development to reduce difficulties in image segmenta-
tion.

3D structures were rendered through Image J. This provides an intuitive visualization of
cathode both the structure and the networks of individual phases. 3D structure analysis and
its conductivity computations are discussed in Chap. 5.
Chapter 5
Electrode Microstructure Metrics

5.1 Introduction

As described in Chap. 2, electrodes are represented by three domains, namely active material, which contains the energy; the carbon domain, which assists in electron flow; and macroscopic pores, which solely conduct ions. Taken together, these domains determine several key factors of the battery system: battery capacity, electronic conductivity, and ionic conductivity. These electrodes’ properties are highly related to microstructure and interactions between the three phases. In order to predict the performance of various battery designs, it is essential to quantify electrode microstructure and transport properties.

In this chapter, we first discuss some metrics to describe electrode microstructure, and compare the resulting statistics from FIB/SEM structures, X-ray structures and macroscopic analysis. We then present algorithms to compute 3D electrodes’ electronic and ionic conductivity from the microstructure. Conductivity sensitivity results are given at the end of the chapter. In Chap. 6, a 3D porous electrode microstructure model is generated using the metrics discussed in this chapter. Even though microstructural analysis and modeling are only applied to the alkaline battery system in this work, these developed techniques are potentially transferable to Li-ion battery systems.
5.2 Structure Metrics

Metrics are used to characterize microstructures and extract information from segmented images obtained using FIB/SEM or X-ray tomography [42, 98]. This work uses volume fractions, two-point correlations, tortuosity, and particle size, which are common metrics used for characterizing microstructure [6, 32, 35, 42, 99, 100].

A more general theory for heterogeneous microstructure description is the N-point probability function. Volume fractions can be considered a 1-point probability. Likewise, two-point correlation functions are simplified versions or subsets of N-point probability functions, which are the probabilities of finding \(N\) points in a volume having particular phase identities and at particular relative locations. For instance, Eq. 5.1 defines a two-point correlation function, which is the probability of finding two voxels (location \(X_1\) and \(X_2\)) of phases \(i\) and \(j\), respectively.

\[
S^{(ij)}_{2}(X_{12}) = \langle I^{(i)}(X_1) I^{(j)}(X_2) \rangle, \\
\tag{5.1}
\]

where angular brackets are an ensemble average. \(I^{(i)}(X_1)\) is the function for \(X_1\) belonging to phase \(i\). The rest follows the same logic. When phase \(i\) is present at voxel \(X_1\), \(I^{(i)}(X_1)\) equals 1. Otherwise, \(I^{(i)}(X_1)\) equals 0. Phases \(i\) and \(j\) can be the active material, carbon, or void domain.

The distance between two voxels \(r\) equals \(|X_1 - X_2|\). When two points coincide, \(r = 0\), the two point function is the probability of finding domain \(i\) at the coinciding voxel, in other words, it is the volume fraction of domain \(i\). When two points are infinitely far away, \(r = \infty\). The correlation of two voxels at infinitely large distances is often found to be insignificant to microstructure. In this work, we use a nearest neighbor function, which is a specific kind of two-point probability function where the distance is fixed to adjacent pixels in an image. The nearest-neighbor distribution function between active materials (A), carbon domain (C), and pore (P) is named as a contact probability in David Stephenson’s dissertation [89].
Another general mathematical technique to describe heterogeneous microstructure is the Fourier transformation. The Fourier transform decomposes a signal (or structure in this work) into the frequencies that make it up. Complicated 2D curves can be described with a series of sinusoidal curves (sine or cosine waves). For example, if earthquake vibrations can be separated into vibrations of different speeds and strengths, buildings can be designed to avoid interacting with the strongest ones. Similarly, if structural data can be represented with oscillating patterns, perhaps the least-important ones can be ignored. We use only a few of the most important ones to represent cathode structure.

We care about metrics that are related to electrode performance because they can help us make performance predictions. Representing cathode microstructure rests on the number of metrics used. The statistics collected in this chapter are used to generate a 3D electrode model. Implementation of higher levels of metrics allows for the capture of more detailed microstructural features. However, the more metrics used to generate this model, the more complex the model will be. Important questions to ask include: how effective is each metric in terms of describing microstructure? How comparable is the conductivity of modeled electrodes to experimental values? These questions are answered in Chap. 6.

This work employs both two-point probability functions (Sec. 5.3) and Fourier transform theory (Sec. 5.4) to describe the microstructure of electrodes.

5.3 Probability Functions

In this section, we look into the volume fraction, nearest neighbor probabilities (surface area), and the particle morphology of segmented electrode microstructures. The statistics of each metric are compared between non-imaging methods, 2D FIB/SEM, 3D FIB/SEM, and 3D X-ray microstructure.

The 2D FIB/SEM image is included in the metrics comparison, which allows us to quantify the statistical difference between 2D and 3D FIB/SEM structures. As explained earlier,
these metrics are used to parametrize the model in Chap. 6. Thus, a comparison between 2D and 3D structures could provide decision-making guidance on whether a 3D structure is necessary for our model parametrization. In particular, prior modeling work was done based solely on a single 2D FIB/SEM image slice.

### 5.3.1 Volume Fraction

The volume fractions of each domain can be calculated from traditional methods based on macroscopic measurements of the mass and volume. The volume fraction can also be calculated directly from segmented images through a pixel/voxel counting method. The sampling volume for each method is different, but the results of both methods can be compared when they originate from the same electrode.

**Gravimetric Method** Commercial alkaline battery cathodes are annular (hollow cylinders); for our research, regular cylindrical pellets were used to simplify fabrication and testing. In a previous study, it was determined that BNB90 additive led to the highest cathode electronic conductivity, when compared to a range of possible carbon additives [9], also see Chap. 7. Here we used BNB90, an expanded graphite made by Timcal [101], as the the conductive additive. The cylindrical pellet preparation process is as follows: (1) Weigh raw material according to dry weight percentage specifications, namely, 5 wt% BNB90 and 95 wt% EMD (Tronox). (2) Add the two raw materials to a closed plastic container and shake for 5 minutes. (3) Transfer about 1.5 grams of mixed raw material into a 20-mm-diameter cylindrical, hardened steel, dry-pressing die set (Across International). (4) Press the die using a hydraulic unit (model 3912 by Carver) to 11 tons (108 kN) by manually increasing pressure. (5) Push the pellet out of die carefully. Lastly, (6) measure its thickness with a digital micrometer (accuracy 1 µm) in 9 locations and calculate the average thickness of the pellet (around 1.49±0.02 mm).
Volume fraction is calculated as follows. The pellet’s overall volume is \( V_t = \pi D^2 T/4 \), where \( D \) is the diameter of the pellet, 20 mm, and \( T \) is the average thickness of the pellet. The volume fraction of EMD and BNB90 is

\[
v_i = \frac{m_i}{\rho_i V_t}
\]

where \( m_i \) and \( \rho_i \) are the weight and density of the individual raw materials in the pellet, respectively. The volume fraction of the pore domain is called porosity \( v_{\text{pore}} = 1 - v_{\text{EMD}} - v_{\text{Graphite}} \).

The calculated volume fractions depend on the densities used in Eq. 5.2. Both EMD and carbon additives demonstrate a nano-porous structure in the particles (see Fig. 2.4 (c) and (d)), which is discussed further in Chap. 7. As illustrated in Fig. 5.1, particles contain closed pores, intra-particle pores and inter particle pores also known as macro pores (not shown in figure). Closed pores exist inside of particles and have no connection to the outside of the pore network. Intra-particle pores exist within particles but connect to macro pores, which are the pores between big particles.

The calculated pore volume fraction \( v_p \) can change, depending on what density \( \rho \) is used for the raw materials. Density \( \rho \) depends on the material volume definition. As shown in Table 5.1, defined volume for crystalline density is crystallite only, which does not include any pores. The crystalline density has the highest density value for all particles. The \( v_p \) using crystalline density in Eq. 5.2 is overall porosity. Defined volume for skeletal density includes crystallites and closed pores; therefore, skeletal density is lower than crystalline density. The \( v_p \) using the crystalline density in Eq. 5.2 contains all pores accessible to electrolyte, including intra particle open pores and macro pores. The defined volume of particle density includes both crystallites and intra particle pores; thus, the \( v_p \) using the particle density in Eq. 5.2 only counts macro pores, and is also known as inter-particle porosity. Table 5.1 lists density values for EMD corresponding to different density definitions [19].

The inter-particle porosity in Table 5.2 is a better metric than the overall porosity to compare the geometric volume fractions determined from cathode microstructures. This is
because it is difficult to quantify the intra-particle porosity from a SEM/FIB image due to low contrast within the EMD, and intra-particle pores are relatively fixed during compression. There is some uncertainty about EMD particle density. Based on previous work done at BYU, a revised value of EMD particle density (3.7 g cm$^{-3}$ rather than the value of 3.3 g cm$^{-3}$ given in Table 5.1) was used to calculate the inter-particle porosities [102]. The particle density of BNB90 is obtained through experiments, as explained in Chap. 6.

Table 5.1: Various density definitions and density values for EMD.

<table>
<thead>
<tr>
<th>Density</th>
<th>Defined volume</th>
<th>Value (g cm$^{-3}$) [19]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline</td>
<td>crystallite only</td>
<td>4.9</td>
</tr>
<tr>
<td>Skeletal</td>
<td>crystallites and closed pores</td>
<td>4.45</td>
</tr>
<tr>
<td>Particle</td>
<td>crystallites plus intra-particle pores</td>
<td>3.3</td>
</tr>
</tbody>
</table>
Table 5.2: Volume fraction calculated using the gravimetric method for alkaline battery cathodes. Skeletal density includes the closed pores within the particles.

<table>
<thead>
<tr>
<th></th>
<th>EMD</th>
<th>BNB90</th>
<th>Pore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Percentage</td>
<td>95%</td>
<td>5%</td>
<td>0</td>
</tr>
<tr>
<td>Skeletal Density (g cm$^{-3}$)</td>
<td>4.45</td>
<td>2.15</td>
<td>0</td>
</tr>
<tr>
<td>Volume Fraction (skeletal density)</td>
<td>68.4%</td>
<td>7.5%</td>
<td>24.1%</td>
</tr>
<tr>
<td>Particle Density (g cm$^{-3}$)</td>
<td>3.7</td>
<td>1.8</td>
<td>0</td>
</tr>
<tr>
<td>Volume Fraction (particle density)</td>
<td>82.3%</td>
<td>8.9%</td>
<td>8.8%</td>
</tr>
</tbody>
</table>

Table 5.2 shows the volume fraction as measured using the gravimetric method with skeletal and particle densities. The presence of internal pores within the EMD and graphite particles is a significant material and microstructural property. For instance, for a BNB90-based cathode, the inter-particle porosity is 8.8%, while the overall porosity is 24.1%; hence, intra-particle porosity accounts for 15.3% of the cathode. In this case, the internal nanoporosity nearly doubles the volume of pores compared to the inter-particle porosity. This suggests that the internal pores of the particles are the main contributor to overall porosity.

2D FIB/SEM  Prior battery microstructure work in our group at BYU was done based solely on 2D FIB/SEM structures [89]. 2D structures are easy to obtain compared to 3D structures. Before any analysis on 2D FIB/SEM structures, an important aspect needed to be considered: estimating the minimal representative volume, which was not addressed in prior work.

We undertook to study uncertainties due to finite sampling of 2D FIB/SEM images. Multiple 2D FIB/SEM images were taken at different spots on the same sample (a 5 wt% BNB90 cathode) to determine the representative size of 2D images. Each 2D FIB/SEM image is 105 $\times$ 115 $\mu$m. Fig. 5.2 (a) shows the volume fraction variations of each domain. The dotted line is the average volume fraction of each domain. The average volume fractions of EMD, BNB90 and macro-pore are 79%, 13% and 8%, respectively.

Fig. 5.2 (b) plots the error in the mean volume fraction against the number of samples. For a 95% confidence interval, the errors in volume fraction mean are calculated as follows:
Figure 5.2: (a) Volume fraction of each domain for multiple sample images on the same cathode (each image is $105 \times 115 \, \mu m$) (dotted line represents the average volume fraction); (b) error in volume fraction at 95% confidence level using Student’s t distribution.
Figure 5.3: (a) 2D FIB/SEM image (234×210 µm) of baseline alkaline battery cathode, (b) Corresponding image after image processing (stretching, segmenting and coarse graining) with node size of 0.5 µm.

\[
Error = \frac{s t}{\sqrt{(n - 1)}},
\]

(5.3)

where \(s\) is the standard deviation of all samples, \(n\) is number of observations of the sample, and the \(t\) value varies with the degrees of freedom and can be found in a \(t\) table of the Student’s \(t\) distribution. As we expected, the more samples we used, the smaller the 95% confidence interval, and the mean value approached the true mean value. In this work, the error in volume fraction is acceptable when the sample size is bigger than four images. The resulting size is around 210 × 230 µm. For an average particle size of 30 µm, each image dimension is 7-8 times the particle diameter, which is considered adequate for particle sampling in other contexts [41, 80].

For a consistent comparison of all metrics between the gravimetric method, 2D FIB/SEM, 3D FIB/SEM and 3D X-ray, one 2D FIB/SEM image of dimensions 210 × 230 µm or larger is desired. Fig. 5.3 (a) is a 2D FIB/SEM image (234×210 µm) of a 5 wt% BNB90 alkaline battery cathode with an overall porosity of 24% (baseline). This is the same cathode used for 3D FIB/SEM imaging. The corresponding fabrication methods are specified in Sec. 5.3.1. Part (b) is the stretched, segmented and coarse-grained image as discussed in Chap. 4, with
Figure 5.4: EMD, graphite and pore volume fractions for each slice of the 3D FIB/SEM image set (baseline cathode).

a pixel size of 0.5 µm. The volume fractions of EMD, BNB90 and pore are 83.3%, 8.3% and 8.4%, respectively for this 2D representative FIB/SEM image. Other metrics of this sample are compared to the 3D FIB/SEM and 3D X-ray tomographies in Sec. 5.3.3.

3D FIB/SEM  Fig. 5.4 shows the volume fraction variation between each slice of the 3D FIB/SEM image set for our baseline alkaline battery cathode. The volume fraction was calculated using the pixel counting method. Overall, the observed EMD volume fraction fluctuated 81±7 %, while the volume fractions of graphite and pore have an inverse relationship. Volume fractions of graphite and pore were 10.2±3.6% and 8.8±2.5%, respectively.

3D X-ray Tomography  The segmentation of 3D X-ray tomography alkaline battery cathode images is discussed in Chap. 4. Because it is difficult to determine proper volume
Figure 5.5: (a) Volume fraction comparison of EMD, BNB90 and pore between various methods for baseline cathode; (b) a slice of segmented X-ray tomographic alkaline battery cathode according to average volume fraction in part (a), black is pore, red is BNB90 and gray is EMD.
fractions of phases for our baseline sample using X-ray tomography, we propose using the average volume fractions obtained with other methods to facilitate segmentation of the 3D data obtained using the X-ray. Fig. 5.5 (a) compares the volume fractions obtained from various methods shown previously. The volume fractions for EMD, BNB90 and macroscopic pore for all methods are 82.2±1.15%, 9.1±0.97% and 8.7±0.23%, respectively. There is a surprisingly good agreement between the gravimetric, 2D FIB/SEM and 3D FIB/SEM methods in terms of volume fraction.

Fig. 5.5 (b) shows a 2D slice of segmented 3D X-ray tomography alkaline battery cathode according to the average volume fraction collected from all other previous methods. The gray threshold values used to segment the 3D X-ray structure into three phases are 72 and 86. Specifically, gray values below 72 are pore, gray values above 86 are EMD, and any value in between is taken to be graphite, because EMD has a higher attenuation coefficient corresponding to a larger gray value. As observed in this segmented X-ray structure, BNB90 coexists with pore, which indicates that the gray values of pore and graphite overlap. Also, BNB90 is assigned to regions at the interface between EMD and pores. This appears to be partly erroneous because it is not observed to this degree in the FIB/SEM images. It is likely caused by the gradient or transition between the gray values of the EMD and pore regions.

5.3.2 Nearest-Neighbor Properties

Nearest-neighbor probabilities are a subset of two-point correlations previously described. They are relatively easy to compute and are used for describing 3D structures [7, 103]. For our system, nearest-neighbor probabilities provide basic correlation information for the three domains, namely EMD (active material), graphite (carbon additive), and pores.

Our 3D electrode structures are divided into cubic voxels with voxel edge length (δ). The voxel length scale directly affects the statistics of the nearest-neighbor properties. Therefore it is important that our computer model (Chap. 6) and experiments be coarse grained to the same δ value. Previous work has established that δ should be smaller than the mean
Figure 5.6: Illustration of lateral nearest-neighbors (green) and diagonal nearest-neighbors (blank) in 2D (a) and 3D (b) space. The center pixel/voxel is marked with red.

particle size of the smallest domain (pore domain here) to keep physical information content at a high level [89]. Here we use $\delta = 0.5\mu m$.

Nearest-neighbor quantities come in two types. Fig. 5.6 (a) illustrates lateral nearest-neighbors (L, green color pixels) and diagonal nearest-neighbors (D, uncolored) of a random center pixel (C, red) in a 2D structure. Part (b) shows lateral nearest-neighbor voxels (the closest voxels in the x, y and z directions, marked with green) and diagonal nearest-neighbor voxels (uncolored) of any random voxel (red). In 3D space, there are six lateral and twelve diagonal nearest neighbors for every voxel. $r$ is the distance between points; thus $r$ for a lateral nearest-neighbor is the pixel or voxel size $\delta$, and the distance between a diagonal nearest-neighbor $r$ corresponds to $\sqrt{2}\delta$ (center-to-center distance). It is worth mentioning that the eight corner voxels of the 3D structure are not included as diagonal nearest neighbors. The distance between the corner voxels and the center voxel is $\sqrt{3}\delta$, which is a greater distance with the two-point probability function than both the lateral and diagonal nearest-neighbors. The two-point probability function at distance $\sqrt{3}\delta$ is unlikely to yield much additional benefit in modeling, but significantly increases computation cost.
Figure 5.7: Lateral nearest neighbor contact probabilities for 2D FIB/SEM, 3D FIB/SEM and 3D X-ray tomography. Node size ($\delta$) for 2D FIB/SEM and 3D FIB/SEM is 0.5 $\mu$m, while the node size ($\delta$) for 3D X-ray tomography is 1.85 $\mu$m. AA represents the fraction of neighboring pixels both belonging to active material domains, AC represents active material and pore domains adjacent to each other, and the remaining labels follow the same logic.

[89]. Also, the 2D structure does not show a two-point probability at distance $\sqrt{3}\delta$, resulting in inconvenience in 2D and 3D structural comparison.

Nearest-neighbor probabilities $g_{ij}(r)$ are normalized from node-to-node (pixel or voxel) contact probabilities $P_{ij}(r)$ relative to the random particle distribution as follows:

$$g_{ij}(r) = \frac{P_{ij}(r)}{v_i v_j}$$ (5.4)

$P_{ij}(r)$ is the observed node-to-node contact probability in the lateral $P_{ij}(\delta)$ or diagonal direction $P_{ij}(\sqrt{2}\delta)$. $P_{ij}(r)$ is calculated by summing all the nearest neighbor contacts of a given type and then dividing by the total number of contacts. $v_i$ is the volume fraction of domain $i$. $v_j$ is the volume fraction of domain $j$ [104]. If the structure is completely random, $g_{ij}(r) = 1$, because the node-to-node contact probabilities $P_{ij}(r)$ equal the probability of having domains $i$ and $j$ at two random spots, which is $v_i v_j$. If $g_{ij}(r)$ is bigger than one, the two particles are favorable and attractive. Otherwise, it is the opposite.
Fig. 5.7 shows the node-to-node contact probabilities $P_{ij}(\delta)$ for 2D FIB/SEM, 3D FIB/SEM and 3D X-ray tomography structures. AA represents the fraction of neighboring pixels/voxels belonging to active material domains, AC represents active material and carbon domains adjacent to each other, and the remaining labels follow the same logic. In contrast to our volume fraction comparison between different tomography structures, larger variations are observed in terms of node-to-node contact probabilities.

### 5.3.3 Particle Morphology

The impact of particle morphology on battery performance has been indicated in many studies [43, 105–107]. Different sizes and shapes result in different diffusion lengths and inter-particle contact resistances. For instance, small particles, which have a high surface area and short diffusion lengths, are generally desirable [107, 108]. However, particles can become too small, causing other processes to become problematic, such as pore tortuosity, side reactions, and degradation. In addition, smaller particles can increase manufacturing costs.

This work is particularly interested in the effect of particle morphology on transport properties. Commonly, computer models of particle-based material morphology use regular shapes, and in particular, spheres. This is partially due to difficulty in measuring and classifying three-dimensional particle shapes [109]. Both the EMD and BNB90 in our cathodes tend to have highly irregular shapes along with a wide range of particle sizes. Therefore, some metrics are needed to describe particle morphology before we quantify its potential effects on electrode transport properties. Particle morphology includes both particle size distribution and particle shape. The material data sheet (MDS) usually includes particle morphology information. FIB/SEM and X-ray tomography images also provide information on domain shapes and sizes. Matlab’s imaging tool box and Image J’s particle analyzer are two commonly used tools for geometric analysis on images [110–115].
Table 5.3: Particle size distributions from material data sheet (MDS).

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>200 mesh (74 µm)</th>
<th>325 mesh (44 µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMD (Tronox AB)</td>
<td>Sieve Mesh Method</td>
<td>90%</td>
<td>60%</td>
</tr>
<tr>
<td>Timcal BNB90 (µm)</td>
<td>Laser Diffraction Method</td>
<td>$D_{90}$</td>
<td>$D_{50}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>85</td>
<td>30-50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D_{10}$</td>
<td>8-15</td>
</tr>
</tbody>
</table>

**Particle Size Distribution**  Laser diffraction (Coulter Counter) is a common experimental tool used to determine the particle size distribution. For the laser diffraction method, limits of $D_{90}$, $D_{50}$, and $D_{10}$ are often used as acceptance criteria, which can be found on the MDS sheet obtained from the material merchant. $D_{90}$ indicates that 90% of particles (mass fraction) are below a certain size. For example, if $D_{90} = 85$ µm, then 90% of the particles in the sample are smaller than 85 µm. The rest follow the same logic. $D_{50}$ is also known as the median diameter or the medium value of the particle size distribution.

Another common method to estimate particle size distribution is by putting the particles through a sieve mesh. Mesh size is defined by the number of openings in the sieve in one inch of screen. As the mesh size increases, the particle size decreases. For example, 325 mesh corresponds to 44 µm (U.S. Standard). One can calculate the percentage of particles that passed through the mesh to determine particle size.

\[
D = \sqrt[3]{\frac{6V}{\pi}},
\]  

(5.5)

where $V$ is the total number of voxels occupied by BNB90 or pore domain in the original 3D volume. Frequency (relative number fraction) is the ratio of domain numbers with a certain equivalent diameter and overall domain numbers found in the 3D structure. Furthermore, the volume fraction of a domain with a certain radius can be obtained by the difference between two successively accumulated volume fractions.

The morphology information extracted from images differs from the information obtained using the two experimental methods discussed above. EMD and graphite particles are well
mixed and then compressed into pellets. Individual particles are then pushed against each other; thus two individual carbon or EMD particles may appear to be one particle in a FIB/SEM image, as shown in Fig. 5.8 (a). Therefore, particles found in FIB/SEM images are identified as domains. In addition, computer algorithms check the neighbors of each voxel (center voxel), and count neighbor voxels as part of one domain object as long as the neighbor voxel has the same identity as the center voxel. As a result, images show only the domain size distribution (DSD), instead of the particle size distribution.

Parts (b) and (d) of Fig. 5.8 are the DSD of BNB90 and pore for 3D FIB/SEM (a) and X-ray structures (c) respectively. In the DSD figure, the red line represents BNB90 and the blue line represents pore. The DSD is presented in two ways: relative number fraction and relative volume fraction. The relative number fraction (dotted-dashed line) represents the frequency of particles with a certain diameter, which is normalized to sum to unity. The relative volume fraction means the weight volume fraction of particles with a certain diameter. The diameter used here is called equivalent diameter.

As shown in Fig. 5.8 (b), the majority of domains are 2 \( \mu m \) in size, but there is one large domain for both BNB90 and pore in the 3D FIB/SEM structure, with an equivalent diameter around 50 \( \mu m \). These domains occupy more than 80 percent of the relative volume fraction for both BNB90 and pore, which means that the majority of the BNB90 and pore domains we observe in 2D FIB/SEM images are all connected in 3D space. However, one thing worth mentioning is that DSD analysis may be biased because of the insufficient size of the 3D FIB/SEM structure or by how it determines connectedness. In contrast, part (d) is the DSD for the X-ray structure, which has a much larger sample size. This DSD shows that the majority of domains are of 5 \( \mu m \) size and have a more even relative volume distribution. The DSD does not show long range domains for BNB90 and pore; this may be due to inexact segmentation of the 3D X-ray structure. In this case, the DSD from the FIB/SEM imagery is more trustworthy because of the detailed segmentation discussed in Chap. 4.
Figure 5.8: Comparison between a volume- and number-based domain size distribution for 3D FIB/SEM (74.5 × 100.5 × 75 µm) and X-ray structures (250 × 250 × 250 µm). Volume weighted BNB90 and pore domain size distributions as well as the equivalent sphere diameter of individual domains were calculated using Matlab.
Table 5.4: Definition of commonly used shape measures.

<table>
<thead>
<tr>
<th>Measures</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspect ratio (AR)</td>
<td>$AR = L/W$</td>
</tr>
<tr>
<td>Circularity (C)</td>
<td>$C = 4A/(PL)$</td>
</tr>
<tr>
<td>Sphericity (S)</td>
<td>$El = \pi^{\frac{1}{3}} (6V^{\frac{2}{3}}/(A))$</td>
</tr>
<tr>
<td>Grain shape factor (GSF)</td>
<td>$GSF = (L/W)^{0.318} P/(2 \sqrt{A})$</td>
</tr>
</tbody>
</table>

**Particle Shape**  
Shape is an extremely difficult property to measure, or even to define in a precise manner. Perhaps this is why there are so many proposed shape measures, none of which has been universally accepted. This work intends to employ a simple method for domain shape characterization. This shape descriptor should be invariant to rotation, scale and translation [117]. Table 5.4 lists some commonly used shape measures, including aspect ratio and roundness (circularity for a 2D structure and sphericity for a 3D structure) [118–121]. For a 2D structure, $A$ means area and $P$ is perimeter. For a 3D structure, $A$ means the surface area and $V$ is the volume.

Aspect ratio is a particle’s longest length divided by its orthogonal distance. One way to calculate aspect ratio is to fit a particle into an ellipse. Fig. 5.9 shows the aspect ratio of the carbon domain using the fitting ellipse method. Calculating the aspect ratio was done using the Image J particle analysis tool. Part (a) is a 2D FIB/SEM image of the baseline cathode. Part (b) outlines and numbers the carbon domain particles (holes in the side of the carbon domain are included). Part (b) excludes points having only one pixel. The particles outlined then are replaced with the best fit ellipses (part (c)), which have the same area, orientation and centroid as the original particles in part (b). The aspect ratio of the carbon domain (part d) is the ratio of the primary and secondary axes of the best fit ellipse.

Fig. 5.9 (d) shows that carbon domains with larger equivalent diameters ($\geq 10 \mu$m) usually have a higher aspect ratio (within range of 3-7). This allows us to quantify the elongated features of carbon domains in the cathode. However, this approach has its own drawback. The best fitted ellipse (1 in part (c)) does not include branch features of the
Figure 5.9: (a) 2D FIB/SEM of baseline (233×211 µm), (b) numbered outlines of the carbon domain in (a), (c) the best fit ellipse of each numbered carbon domain in (b), (d) the aspect ratio of the carbon domain’s fitted ellipse in (c).

outlined carbon domain (1 in part (b). Instead, the fitted ellipse presented a low aspect ratio.

**Volume-metric Surface Area**  
In battery modeling work, surface area per volume $a$ has often been used and considered as a function of both particle size and shape. $a$ directly affects the relative number of the reaction centers. For a spherical particles, $a = 3/r$ ($r$ is radius of sphere), while particles with rough surfaces would have larger $a$ value. A higher
Figure 5.10: Parameter $a'$ of BNB90 and pore particles observed in Fig. 5.9 (a).

$a$ value leads to a larger number of reaction centers, which is a desirable cathode feature. Similarly, parameter $a'$ is defined as perimeter per area for 2D structures.

Fig. 5.10 shows $a'$ value of the BNB90 and pore domains we observed in the 2D FIB/SEM images (Fig. 5.9 (a)). Fig. 5.10 also excludes points having only one pixel. As expected, domains of larger equivalent diameter have a low $a'$ value and domains of smaller equivalent diameter have a high $a'$ value, because $a'$ has an inverse relationship with domain diameter. Fig. 5.10 also shows that domains of small equivalent diameter have an $a'$ value similar to that of a circle, while domains of large equivalent diameter have a much higher $a'$ value compared to that of a circle. This indicates that large particles are not at all spherical in shape. The majority of BNB90 domains show a shape factor $a'$ of 1 [$\mu$m$^2$/µm$^3$], even though there are fewer BNB90 domains. In contrast, over 90% of pore domains at equivalent diameters are under 5 µm. The shape factor $a'$ is at a range of 1-6 [$\mu$m$^2$/µm$^3$].
5.4 Fast Fourier Transformations

Another popular method to describe heterogeneous structure uses the Fourier transformation. Fourier transforms are often used to analyze finite, repetitive structures [122, 123]. The Fourier transform decomposes an image into its wave functions (sine and cosine components). The image are represented using the Fourier wave vector or reciprocal lattice domain. In the Fourier space, each point represents a particular wave vector contained in the spatial or real domain image (FIB/SEM). The number of wave numbers corresponds to the number of pixels in the spatial domain image.

Only preliminary results were given to show the correlation between Fourier transform coefficients and structures. The Fourier transform method is not implemented in model parametrization due to time constraints. William Lange from BYU’s Electrical and Computer Science Engineering Department developed the computer code for this fast Fourier transformation study.

The three-phase structure is first filtered into three binary structures containing only active material (A), carbon (C) and pore (P). Fourier transformation structure factors are performed for each domain. In practical applications, Fourier transformation usually refers to discrete Fourier transforms (DFT). The DFT is the sampled Fourier transform and therefore does not contain all wave vectors that form an image, but only a set of the sample which is large enough to fully describe the spatial domain image.

\[ F(k) = \frac{1}{N} \sum f(r_j) e^{-i kr_j} \] (5.6)

where \( r \) is the position vector of the 3D cathode structure \( r = \begin{bmatrix} m_1 \\ m_2 \\ m_3 \end{bmatrix} \delta; \) \( m_1, m_2, m_3 \) are independent integers; and \( \delta \) is the node size of the 3D structure in units of \( \mu \text{m} \). \( f(r) \) is a dimensionless Fourier coefficient where the value is either 1 or 0. For instance, \( f(r) \) equals
1 if the identity at the \( r \) position belongs to active material for the active binary structure. \( N \) is the number of pixels or voxels. \( i \) in the exponent is an imaginary number and \( j \) is the voxel index.

Wave vector \( \mathbf{k} \) is a reciprocal lattice vector for a 3D structure of mutually orthogonal dimensions \( L_1, L_2 \) and \( L_3 \) in units of \( \mu m \) in our case. We obtain the set of wave or reciprocal lattice vectors

\[
\mathbf{k} = 2\pi \begin{bmatrix} \frac{n_1}{L_1} \\ \frac{n_2}{L_2} \\ \frac{n_3}{L_3} \end{bmatrix},
\]

where \( n_1, n_2, \) and \( n_3 \) are independent integers. Wave number \( k \) is the absolute value of the wave vector \( \mathbf{k} \), \( k = |\mathbf{k}| \).

Direct DFT computation directly requires operations that scale \( N^2 \), where \( N \) is the number of pixels or voxels. Therefore, it is often too slow to be practical, especially for long data sets where \( N \) may be in the thousands or millions. Fast Fourier transform (FFT) is a way to compute the same result more quickly by reducing the order of arithmetic operations to \( N \log N \) [124–126]. This work implements the FFT Cooley–Tukey algorithm preprogrammed in Matlab [127, 128].

\( F(\mathbf{k}) \) can provide domain correlation at different wave numbers. \( F(\mathbf{k}) \) contains real and imaginary terms. In an image structure, we only care about the relative location rather than the absolute location in real space. Therefore, phase angle information in imaginary terms is unnecessary, while real terms provide domain correlations, which are calculated through multiplying \( F(\mathbf{k}) \) by its complex conjugate. For example, the correlation between the active material and carbon additive (BNB90) \( C_{AC} \) is

\[
C_{AC}(\mathbf{k}) = \sqrt{\frac{|F_A(\mathbf{k}) \cdot F_C^*(\mathbf{k}) + F_C(\mathbf{k}) \cdot F_A^*(\mathbf{k})|^2}{2}},
\]

(5.8)
where $F_A(k)$ is the Fourier transform in terms of active material binary images using the fast Fourier transform function $\text{fftn}$ in Matlab, and $F_A^*(k)$ is the complex conjugate of $F_A(k)$ using the $\text{conj}$ function in Matlab. The rest follow the same logic. $F_A(k)$ is normalized by structure size so that the magnitudes of domain correlations are irrelevant to the structure size.

Fourier correlation could allow us to identify periodic structures in the cathodes. One can identify peaks in the correlation functions that identify characteristic wave numbers. However, there is an upper cutoff bound of $k$ one can use. In other words, the Fourier correlation between AA, CC and PP decreases with the wave number, which means a larger wave number does not carry as much significant information as a small wave number does. Therefore, the least important wave numbers can be ignored [124, 129, 130].

The Fourier correlations were first validated at the wave number zero, where the correlation $C_{AA}(0)$, $C_{CC}(0)$, and $C_{PP}(0)$ corresponds to the volume fractions of the active material (A), carbon (C) and pore (P) domains.

**2D FIB/SEM vs. 3D FIB/SEM vs. 3D X-ray** Fig. 5.11 plots Fourier transform self-correlation against the wave numbers of the 2D FIB/SEM, 3D FIB/SEM and 3D X-ray structures. A characteristic wavelength is $r = 2 \pi / k$, where $k$ is the significant wave-number in Fourier space. Fourier correlations of 2D FIB/SEM and 3D FIB/SEM show that the most significant correlations are at wave numbers $0.15-0.2 \mu m^{-1}$, which corresponds the significant wavelength around 30-40 $\mu m$. This is the median size for both EMD and graphite domains, which suggests that domain size and interactions are likely the most effective parameters to describe cathode microstructure. Moreover, self-correlation peaks of the 3D FIB/SEM structure at wave numbers from $0.15 – 0.2 \mu m^{-1}$ are more obvious compared to those of the 2D FIB/SEM structure, while the self-correlation of the 2D FIB/SEM structure presents another important peak near wave number zero. Wave number zero corresponds to the
volume fraction of the domains. This suggests that volume fraction is another significant parameter, especially if sample size is insufficient.

Fourier correlations of 3D X-ray structures have a smaller magnitude compared to those of FIB/SEM structures and show a clear peak around 0.05 $\mu$m$^{-1}$. This corresponds to a significant wavelength of around 125 $\mu$m, which is the length of 2-3 EMD or BNB90 particles. This suggests that particle neighbor probability could be another significant structure parameter. At the same time, periodic structure features could be artificially shifted in the 3D X-ray because X-ray tomography cannot definitively detect carbon additive.
Figure 5.12: FIB/SEM image of (a) BNB90 (103×112 µm) and (b) graphene (120×140 µm). Gray is EMD, black is carbon, and white is pore.

One thing worth clarifying is that the right-end peaks shown in the Fourier correlation in Fig. 5.11 were artifacts from our computer Fourier transform algorithm.

**BNB90 vs. Graphene** BNB90 and graphene cathodes exhibited the highest conductivities in our experimental work[9]. Both of these additives can be considered expanded graphite and more details are discussed in Chap. 7. Fig. 5.12 shows the segmented FIB/SEM images of the BNB90 and graphene cathodes. Note their distinctive microstructure. Fourier transform analysis was attempted on the two cathode structures because it could potentially be used as a metric for modeling cathode microstructure [131].

Fig. 5.13 shows the self-correlation for the three phases of the two cathodes. First, $C_{AA}$ shows a characteristic wave number around 0.15 µm$^{-1}$ for the BNB90 cathode and 0.5 µm$^{-1}$ for the graphene cathode, which means that significant EMD wavelengths for the BNB90 and graphene cathodes are around 40 and 12 µm, respectively. This agrees with Fig. 5.12, where the EMD domain size is relatively small compared to that of the BNB90 cathode.
Figure 5.13: Fourier self-correlation for the three phases of the BNB90 (left panels) and graphene (right panels) cathodes shown in Fig. 5.12. Node size 0.5 µm. $C_{AA}$ means the Fourier correlation between active domains, $C_{CC}$ means Fourier correlation between BNB90 domains, and $C_{PP}$ means Fourier correlation between pore domains.
Second, a much stronger \( C_{CC} \) correlation around 0.1 \( \mu m^{-1} \) was observed for the graphene cathode, meaning the carbon domains correlate around the 60 \( \mu m^{-1} \) length scale. This is consistent with Fig. 5.12, considering the graphene cathode is mostly covered by carbon domain (graphene). Third, there are few peaks in the \( C_{PP} \) correlation for the carbon domain in the graphene cathode. This may be due to the lack of periodicity or scattered nature of the pore domain.

On the other hand, there is notable noise for the self-correlations in Fig. 5.13, so the correlation peaks are not as obvious as they could be. One could sample a larger portion of the cathode to reduce the noise we observed here. Overall, Fourier transform could be an alternative metric for a porous electrode model, but additional work is needed.

5.5 Computing Conductivities of 3D Cathodes

Effective electrode transport properties, including electronic and ionic conductivity, are functions of domain intrinsic properties, microstructural configuration and boundary conditions. This section discusses the computation of both the electronic and ionic conductivities of 3D FIB/SEM and 3D X-ray structures. The results are compared to experimentally measured values.

Often, an artificial or dimensionless intrinsic conductivity value is assigned to each domain [7, 32]. However, it is more meaningful to predict the influence of microstructure and morphology on transport properties with a reasonable or realistic input value. Therefore, we experimentally measure intrinsic ionic conductivity in addition to using intrinsic electronic conductivity values from literature.

5.5.1 Intrinsic Conductivity

Ideally, intrinsic particle conductivity is the conductivity of a single-crystal particle. However, it is challenging to measure single-particle conductivity because of the relatively large contact
Table 5.5: Domain conductivities of alkaline battery components: BNB90, EMD and macro-size pores (assuming 8.7 M KOH).

<table>
<thead>
<tr>
<th>Domain conductivity</th>
<th>BNB90</th>
<th>EMD</th>
<th>Macro pore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic (S m(^{-1}))</td>
<td>1.4(\times)10(^5)</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>Ionic (S m(^{-1}))</td>
<td>0.03</td>
<td>4</td>
<td>62</td>
</tr>
</tbody>
</table>

resistance between a single particle and external electrical probes. Initially, we made efforts to measure a single particle with a nano-probe (5 \(\mu\)m) under a microscope, but the results were not consistent, possibly due to contact resistance and inaccurate particle geometry estimation under the microscope.

More commonly, the intrinsic electronic conductivity of particles is estimated in a pellet subjected to high pressure. It is reported that the electrical conductivity of graphite is around 1.4\(\times\)10\(^5\) S m\(^{-1}\), specifically, 2.6\(\times\)10\(^6\) S m\(^{-1}\) parallel to the basal plane, and 10\(^4\) S m\(^{-1}\) perpendicular to the basal plane [132–134]. These conductivity values are validated over a range of thicknesses (0.25 nm to 2.5 \(\mu\)m). The conductivity is relatively insensitive to temperature. The electrical conductivity of EMD is reported to be 1-2 S m\(^{-1}\). This measurement was done by making pellets under unspecified high pressure [18].

The ionic conductivity of KOH at 8.7 M is 62 S m\(^{-1}\) [135]. Theoretically, solid EMD and graphite are not significant ion conductors compared to liquid electrolytes; however, both EMD and BNB90 have a nano pore structure. Therefore, the EMD and graphite domains shown in the segmented 3D structure actually conduct ions because of intra-particle pores. It is important to measure the corresponding ionic conductivity of the EMD and graphite domains. Intra-particle porosity of the EMD domain does not change so long as no particles collapse, while the intra-particle porosity of the BNB90 domain varies because BNB90 is very deformable. In other words, the ionic conductivity value for BNB90 depends on the intra-particle porosity of BNB90.

Some experiments were done in our research group to approximate the ionic conductivity of the EMD and BNB90 domains in cathodes. First, we made pure EMD and BNB90 pellets while attempting to make inter-particle porosity close to zero. Pure EMD was compressed
under 11 metric tons 50 times and left standing under pressure over a day to accomplish this. In a typical case, the resulting EMD pellet had a density of 3.37 g cm$^{-3}$, which is in the particle density range listed in Table 5.1. Therefore, we can assume that the EMD pellet was well compacted and only intra-particle pores were left in the pellet. The pure BNB90 pellet was compressed under less force in order to achieve the same amount of intra-particle pores that would be present in the BNB90 domain of the baseline alkaline battery cathode. The corresponding density of such a pure BNB90 pellet was 1.69 g cm$^{-3}$.

Tortuosity (defined in terms of Eq. 5.9 below) of each pellet was measured, as will be discussed in a forthcoming publication by Mehdi Forouzan [136]. Domain ionic conductivity is given by

$$k = \frac{k_{\text{KOH}} \epsilon}{\tau}$$  \hspace{1cm} (5.9)

where $\epsilon$ and $\tau$ are the intra-particle porosity and tortuosity of pure EMD and BNB90 pellets, and $k_{\text{KOH}}$ is the ionic conductivity of KOH at 8.7 M. Table 5.5 summarizes all domain conductivity values from both the literature and our experiments.

5.5.2 Computing Algorithm

Finite volume methods have been developed to compute 3D microstructure properties [7, 80]. Our conductivity computing model mainly implements the finite volume method and periodic boundary condition to compute the effective conductivity of the bulk electrode structure.

Fig. 5.14 illustrates the finite volume method used to compute effective conductivity. First, it imposes an external potential field $\nabla \phi^{\text{ext}}$ across the voxel grid. Then, it solves for the deviation of the potential distribution $\phi^{\text{dev}}$ for each voxel, based on the conservation of current. $\phi^{\text{dev}}$ is local deviation relative to average potential gradient $\nabla \phi^{\text{ext}}$.

Current flows from voxel $I$ to voxel $J$: 

110
\[ I_{J \rightarrow I} = k_{ij}(\phi_{J}^{\text{dev}} - \phi_{I}^{\text{dev}} + \nabla \phi^{\text{ext}} \cdot S_{IJ}), \quad (5.10) \]

\( S_{IJ} \) is a unit direction vector between voxels \( I \) and \( J \). The product is \( \nabla \phi^{\text{ext}} \cdot S_{IJ} \) indicates that the potential difference between voxels is caused directly by the external field.

\[ k_{ij} = 2 k_i k_j / (k_i + k_j), \quad (5.11) \]

is the harmonic mean for the conductivity of domains \( i \) and \( j \). The current flowing into node \( I \) must be conserved, which means the sum of \( I_{J \rightarrow I} \) for all neighbors \( J \) to node \( I \) is zero. There is one such conservation equation for each node or voxel. Solving all of these simultaneously allows one to determine the deviation of the potential distribution \( \phi^{\text{dev}} \) on the 3D grid.

Figure 5.14: Illustration of finite volume method used to solve deviations of potential distribution \( \phi^{\text{dev}} \) on a 3D grid and to solve 3D matrix effective conductivity.
To calculate effective conductivity, one must compare the total current passing through the grid to the external driving potential. Current $I^{\text{tot}}$ is calculated through a plane normal to $\nabla \varphi^{\text{ext}}$. To check the answer for convergence, we chose total current $I^{\text{tot}}$ of the middle and end planes. The computer algorithm alerts the user when the two current values differ from each other by more than 5% across the electrode structure. The middle and end planes are chosen for the two current values. The effective conductivity of the 3D matrix is calculated with the following formula:

$$K^{\text{eff}} = \frac{I^{\text{tot}}}{A |\nabla \varphi^{\text{ext}}|}$$

(5.12)

where $A$ is the cross section area of the plane.

The periodic boundary condition indicates that an external potential field $\nabla \varphi^{\text{ext}}$ extends across the voxel grid, where one side of the voxel grid could connect to the opposite side of the voxel grid. In contrast, the insulating boundary condition sets a constant potential on one side of the voxel grid and 0 voltage on the other side.

### 5.5.3 Algorithm Validation

A dummy structure as shown in Fig. 5.15 is used for validating the conductivity computing algorithm. The following volume fractions were used: 10% BNB90, 80% EMD, and 10% pore. In one case, the three domains are in parallel; in another case, they are in series, as discussed in Chap. 2. The effective conductivity is given by Eq. 2.7 when the three domains are in parallel, or by Eq. 2.8 when the three domains are in series.

Table 5.6 compares effective conductivities from analytical solutions using Eqs. 2.7 and 2.8 and the conductivity computation algorithm. Domain conductivities in Table 5.5 are used for computation of the dummy structure’s effective conductivity. The results are identical, which validates our conductivity computation algorithm. The expected effective electronic conductivity values in parallel and in series are around $1.4 \times 10^4 \text{ S m}^{-1}$ and an infinitely small...
Figure 5.15: Model validation with a dummy structure composed of the three domains in a simplified series or parallel structure; red is graphite, green is EMD and blue is pore.

Table 5.6: Effective conductivities of 3D dummy structure (S m$^{-1}$).

<table>
<thead>
<tr>
<th>Effective conductivity</th>
<th>Analytical Parallel</th>
<th>Series</th>
<th>Computation algorithm Parallel</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic</td>
<td>1400.12</td>
<td>0</td>
<td>1400.12</td>
<td>0</td>
</tr>
<tr>
<td>Ionic</td>
<td>9.4</td>
<td>0.28</td>
<td>9.4</td>
<td>0.28</td>
</tr>
</tbody>
</table>

number, respectively. At the same time, the expected effective ionic conductivity values in parallel and in series are around 9.41 S m$^{-1}$ and 0.28 S m$^{-1}$, respectively. This means that effective electronic and ionic conductivity values are favorable if the graphite and pore layer structures align tangentially with the direction of current flow.

Improved electronic and ionic conductivity are necessary, yet insufficient in optimizing cathode microstructure. Conductivity is maximized where graphite, pore and active material are stacked in a sandwich structure; however, batteries fabricated with such a structure would be useless because the three phases have poor connectivity where graphite and active material are separated by pore. Thus the graphite is of no use and electrons have really limited access
to reaction centers. Another metric, such as a three-phase boundary (electrons, ions in the pore and active material), would further enhance design process in microstructure.

5.5.4 Conductivity Computing Results

Fig. 5.16 contains 3D microstructures for effective conductivity computation. Part (a) is the 3D FIB/SEM structure of 4.3 wt\% BNB90 at 27\% overall porosity. Part (b) is the 3D FIB/SEM structure of 5 wt\% BNB90 at 24.1\% overall porosity. Part (c) is the 3D X-ray structure of 5 wt\% BNB90 at 24.1\% overall porosity.

Boundary Conditions  The effective conductivities were computed with periodic and insulating boundary conditions for the two 3D FIB structures in Fig. 5.16. The ionic conductivity result difference between the two boundary conditions for both 3D FIB structures is negligible, whereas effective electronic conductivity with the insulating condition applied is 20-30\% higher than with the periodic condition applied. Note that FIB/SEM structures contain relatively few particles while experimental transport measurements were performed for full-size pellets. Particularly, the equivalent diameter for BNB90 domain is around 50 µm compared to FIB/SEM structures that only modestly exceed this length. Thus our FIB/SEM structures are not necessarily sufficient to compute reliable average electronic conductivity. In addition, there is also a larger deviation in the mean values between each of the three axes using the insulating boundary condition. Hence, conductivity was computed using the periodic condition for the rest of this work.

Computed vs. Experimental Conductivity  Table 5.7 shows the conductivity comparison between the 3D structure computations (using the domain conductivities shown in Table 5.5) and the corresponding experimental measurements. Experimental measurements can be found in Ref. [9, 136].

The computed electronic conductivities of the two 3D FIB/SEM structures are much higher than the experimental values, which implies that the contact electronic resistance
Figure 5.16: 3D microstructures of electrodes for conductivity computation: (a) 3D FIB/SEM structure for 4.3 wt% BNB90 (74.5 × 100.5 × 75 µm) with node size δ = 0.5 µm, (b) 3D FIB/SEM structure for 5 wt% BNB90 (76.5 × 173.5 × 65 µm) with node size δ = 0.5 µm, (c) 3D X-ray structure of 5 wt% BNB90 (250 × 250 × 250 µm) with node size δ = 1.85 µm.
Table 5.7: Conductivity comparison between computing 3D microstructure (Fig. 5.16) and experimental measurements. The experimental conductivity values were measured in the Y direction, which is also the cathode compression direction. The Z direction is the FIB/SEM slice milling direction.

<table>
<thead>
<tr>
<th>Effective conductivity</th>
<th>Electronic (S m(^{-1}))</th>
<th>Ionic (S m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Computation</td>
<td>Experiment (Y)</td>
</tr>
<tr>
<td>4.3 wt% BNB90 (3D FIB/SEM)</td>
<td>X (422.1±2.1)</td>
<td>Y (544.6±3.6)</td>
</tr>
<tr>
<td></td>
<td>Average (424.4±56.1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 wt% BNB90 (3D FIB/SEM)</td>
<td>X (983.8±4.9)</td>
<td>Y (705.5±55.9)</td>
</tr>
<tr>
<td></td>
<td>Average (614.5±199.0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 wt% BNB90 (3D X-ray)</td>
<td>X (5.5±1.4)</td>
<td>Y (5.3±1.2)</td>
</tr>
<tr>
<td></td>
<td>Average (5.0±0.3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

between domains is significant. Contact resistance exists at the interface of particles. In contrast, the computed results for ionic conductivity are slightly overestimated compared to experimental values, which may be due to inter-domain resistance between bulk liquid and pellets. The computed conductivity of the 3D X-ray structure is much less than that of both the FIB/SEM structure and the experimental values. This is likely due to our inaccurate segmentation of the X-ray structure in Chap. 4. For this reason, the 3D X-ray structure was not used for any further analysis.

Assuming particle-to-particle contact resistance fully accounts for the conductivity differences between the computed and experimental values, contact resistance could make up approximately 70% of overall electronic resistance. Ionic pathways do not have a corresponding problem. The above facts could be explained by the transport mechanisms associated with electrons and ions. In order for electrons to travel from one particle to another, they
must hop between particles at the particle interface. Electrons can transfer effectively only in nm scale, so the electrons’ hopping resistance between particles is significant for electronic conductivity [137, 138]. This suggests that types of graphites that provide intimate inter-particle connections could be a more important factor to consider than just the intrinsic domain conductivity of the particles.

**Fitted Domain Conductivity**  One way to account for the contact or interfacial resistance in the 3D microstructure conductivity computations is to build the contact resistance into intrinsic domain conductivity by regressing domain transport properties using experimental conductivity values and the cathode’s 3D microstructure. Specifically, conductivity computation results can be matched with experimental values in the Y direction (the experimental conductivity values were measured in the Y direction). The two FIB/SEM structures are used to fit the domain conductivity values, which are listed in Table 5.8. This was done by adjusting the electronic conductivity of graphite and the ionic conductivity of EMD. The newly fitted domain conductivity is then used as the domain conductivity during stochastic modeling validation and prediction.

Table 5.8: Fitted domain conductivities of alkaline battery components: graphite, EMD and macro-size pores.

<table>
<thead>
<tr>
<th>Domain conductivity</th>
<th>Graphite</th>
<th>EMD</th>
<th>Macro pore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic (S m⁻¹)</td>
<td>3×10⁴</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>Ionic (S m⁻¹)</td>
<td>0.03</td>
<td>2</td>
<td>62</td>
</tr>
</tbody>
</table>

Alternatively, one could include the contact resistance in the harmonic mean conductivity (Eq. 5.11) of the AC domain. Since the AC interfaces change with electrode microstructures, the contact resistance of the microstructure varies with the amount of AC interfaces. Thus, adding contact resistance to the harmonic mean conductivity could account for the interface variation of AC interfaces, while building contact resistance into domain resistance does not cause effective conductivity to self-adjust to the number of AC interfaces. At the same time, including the contact resistance within harmonic mean conductivity would assume no contact
resistance between AA and CC voxel pairs. In reality, contact resistance does exist between AA and CC particle interfaces.

**Effective Medium Theory** The Bruggeman relation is a well-known effective medium theory used to approximate the effective conductivity of porous electrodes [39, 139, 140]. The Bruggeman relation assumes the macroscopic system is homogeneous and thus the effective conductivity is treated as a function of the volume fractions. Commonly, $k_{\text{eff}} = k_{\text{in}}\varepsilon^{1.5}$ is used to approximate the effective ionic conductivity of porous electrodes, where $k_{\text{in}}$ is the ionic conductivity of the electrolyte, and $\varepsilon$ is the overall porosity of the electrode. Here the overall porosity is 24.1% for the 3D FIB/SEM structure in Fig. 5.16 (b). Thus, the approximated effective ionic conductivity of the 3D FIB/SEM structure is 7.3 S m$^{-1}$, which is much higher than our computed or experimental results (2.64 S m$^{-1}$). This comparison suggests that the conductivity computation of 3D structures is useful to accurately calculate the effective conductivity of electrodes. In addition, recent experimental results also indicate that the complexity of the porous electrode microstructure induces effective conductivity values that greatly deviate from the classical Bruggeman ideal [141, 142].

**Anisotropic Properties** As shown in Table 5.7, the two 3D FIB/SEM structures show anisotropic properties in both electronic and ionic conductivity. Electronic conductivity displays strong anisotropic properties, for example, electronic conductivity in the X direction is about six times higher than in the Y direction for the baseline structure (FIB/SEM), whereas the ionic conductivity of one direction is only slightly higher than that of the other. Anisotropic properties of ionic conductivity were also observed in experimental results. Ionic conductivity orthogonal to the direction of compression was found to exceed the conductivity parallel to the compression. The conductivity results in Table 5.7 were computed with domain conductivity (Table 5.5) instead of fitted domain conductivity (Table 5.8), so anisotropic properties of effective conductivity in Table 5.7 are amplified. Fig. 5.17 shows
the anisotropic properties of conductivities using the fitted domain conductivity, and voxel size $0.5 \, \mu m$ corresponds to FIB/SEM structures in Fig. 5.16.

Figure 5.17: (a) Effective conductivity versus voxel size for Fig. 5.16 (a), and (b) effective conductivity versus voxel size for Fig. 5.16 (b). Error bars are the standard deviations of the mean for the three coordinate directions. The lines connecting points are to guide the eye.
Coarse-Grain Effects  Conductivity computation for a full-size FIB/SEM structure (voxel size 0.5 µm) in Fig. 5.16 is somewhat time consuming (around 1-2 days for one sample). For the purpose of rapid computation, the effective conductivities of the two 3D FIB/SEM structures are computed at a range of coarse-grained voxel sizes, as shown in Fig. 5.17.

Electronic conductivity rapidly decreases as voxel size increases, and ionic conductivity gradually decreases or remains the same as voxel size increases, which indicates that graphite has a fine structure in the sub-micron scale which contributes significantly to effective electronic conductivity. Thus, a higher resolution (voxel size less than 0.5 µm) is desired for definite conductivity computation. However, increasing resolution would exponentially increase computation costs as well, especially since computing 3D FIB/SEM structure conductivity at the current resolution is already quite time consuming. Hence, there is a trade-off for microstructure resolution to effectively compute cathode conductivity.

Conductivity Sensitivity  We are interested in the sensitivity of pellet effective conductivity to domain conductivity. The domain conductivity of components could vary due to raw material types or manufacturing conditions, such as different carbon additives (electronic conductivity $10^2 - 10^5$ S m$^{-1}$), altering the intra-particle porosity of EMD (ionic conductivity is around $1.5 - 12$ S m$^{-1}$ with respect to EMD 10%–40% intra-particle porosity), and mixing carbon powder into EMD to form EMD aggregates ($0.1 - 15$ S m$^{-1}$).

Fig. 5.18 shows effective conductivity sensitivity with the conductivity of the three domains, where the domains' conductivities are presented relative to their fitted domain conductivities (Table 5.8). The 3D structure of the baseline cathode (Fig. 5.16 (b)) was coarse grained by a factor of two for the sensitivity test in order to save on computation time. Both electronic and ionic conductivity are quite sensitive to the EMD domain conductivity value, likely because it occupies a large volume fraction.
Figure 5.18: (a) Effective electronic conductivity sensitivity (horizontal axis is the domains electronic conductivity relative to the fitted domain electronic conductivity in Table 5.8), (b) effective ionic conductivity sensitivity (horizontal axis is the domain’s ionic conductivity relative to the fitted domain ionic conductivity in Table 5.8).
Improved EMD electronic and ionic conductivity would therefore be most beneficial to electrode overall conductivity. One could mix a small amount of carbon powder (such as small graphene flakes) in with the EMD particles to improve EMD domain electronic conductivity. One could also increase the intra-particle porosity of the EMD or electrolyte ionic conductivity to raise the EMD domain ionic conductivity.

Graphite domain conductivity could also greatly influence overall electronic conductivity. Moreover, Fig. 5.18 (a) suggests that anisotropic properties are likely magnified by increasing graphite domain conductivity, since larger error bars (deviation from the mean value of conductivity in three directions) are observed as graphite domain electronic conductivity changes. On the other hand, effective ionic conductivity is not strongly correlated with graphite domain ionic conductivity.

It is worth mentioning that changing certain electrode design factors could impact more than one domain conductivity. For example, when changing electrolyte ionic conductivity, EMD and graphite domain conductivity is also modified. Another example is changing the porosity of EMD, which causes both the electronic and ionic conductivity of the EMD domain to change.

5.6 Conclusion

Electrode microstructure metrics, including volume fraction, nearest neighbor probabilities, particle morphology, Fourier transform coefficient, and effective conductivities have been discussed. The statistics of each metric were compared between non-imaging methods, 2D FIB/SEM, 3D FIB/SEM, and 3D X-ray microstructure images. X-ray structure was found to be less useful for quantitative analysis in this study because the three domains could not be accurately identified. The following conclusions can be made:
First, a minimal representative volume was estimated, namely that each image has dimensions of at least 7-8 times the particle median diameter for adequate cathode sampling, in agreement with the work done in other scientific contexts [41, 80].

Second, there was a good agreement between the gravimetric method, 2D FIB/SEM and 3D FIB/SEM methods in terms of observed domain volume fractions. However, a larger difference is observed between nearest-neighbor probabilities and the aforementioned methods.

Third, particle morphology was interpreted using domain size distribution, aspect ratio and $a$. A domain size distribution algorithm was developed for 2D and 3D structures. Large volume fractions of the BNB90 and pore domains were found to be connected in the 3D structure. Aspect ratio was examined for the carbon domain in the 2D FIB/SEM structure, where large carbon domains $(\geq 10 \, \mu m)$ show high aspect ratio in the range of 3-7. In addition, surface area per volume $a$ (3D structure) and perimeter per area $a'$ (2D structure) were used as descriptors for combined domain size and shape. Corresponding computer algorithms were developed for use in this work.

Fourth, Fourier transform coefficients were used to describe particle long-range correlations and distinguish the cathode microstructure of different carbon types. Self-correlations were tested on both 2D and 3D structures. It was found that volume fraction, domain size and particle interactions within a size range equal to 2-3 EMD particles were likely the most effective parameters to describe cathode microstructure. Fourier transform could be an alternative metric for a porous electrode model, but additional work is needed.

Lastly, the effective conductivity of 3D structures was computed using the finite volume algorithm. Particle contact resistance appears to be important and made up approximately 70% of overall electronic resistance in our 3D FIB/SEM structures, assuming carbon domain conductivity from literature is correct. Domain conductivities were fitted with a combination
of the two 3D FIB/SEM structures and experimental conductivity values. According to conductivity sensitivity results, effective conductivity is sensitive to the level of coarse-graining and domain conductivity.
Chapter 6
Stochastic Grid Model

6.1 Introduction

A realistic microstructure model allows the transport properties of cathodes to be predicted with different structural configurations. We seek a model that uses a small set of fundamental parameters (such as the metrics from Chap. 5) to generate a porous microstructure that mimics the configuration of real electrodes. Once the model microstructure configuration is generated, we can compute its transport properties using the algorithms discussed in Sec. 5.5.

The stochastic grid (SG) model is based on the Monte Carlo numerical method and node swapping techniques, which were introduced in Chap. 2. The SG model divides the electrode into many nodes on a grid, each of which represents a small volume that can be occupied by active material, carbon or pore. A core step of the SG model is called the Metropolis algorithm, in which a swap between randomly selected nodes is accepted or rejected based on the relative probabilities of the initial and proposed configurations. When a swap is made, the phase identities of the two nodes are exchanged. This node swap technique naturally conserves the volume fraction of each phase.

In addition, SG model can explore design features not possible with experiments. For instance, one of the modeling tasks is to identify the characteristics of volume-efficient carbon additives in cathodes. Volume-efficient carbon additives means that a cell can pack less carbon additives and more active material (more capacity) while sustaining the electrode effective conductivities. We can run the SG model with a particular or artificial carbon
morphology and predict its conductivity. Therefore, a microstructure model could permit quick selection of advantageous raw material characteristics.

The SG model is only applied to alkaline battery cathodes in this work. In particular, the model is used to determine changes in the level of transport property performance due to raw material changes (graphite and EMD). Although alkaline battery technology has been used since the 1960s, few research efforts have been made to model the microstructure of alkaline batteries [143, 144].

This chapter first reviews existing electrode models inside and outside our research group. Then, the SG model developed in our group is adapted to the alkaline battery system. Additional algorithms are added to improve the SG model microstructure. The improved model is validated with cathodes of different carbon types and mass fractions. Then the validated model is used to predict the microstructures of various domain morphologies and their corresponding conductivities. The chapter concludes by considering the effect of microstructure changes on overall cell performance.

6.2 Background

The stochastic simulation technique is capable of generating random 3D porous microstructures using low-order statistical information such as volume fraction and nearest neighbor interactions. This technique is used in multiple disciplines such as fluids, mineral processing, and battery electrodes for porous media simulation [34, 42, 75, 100, 145–148]. Particularly, for modeling porous battery electrodes, Thiedmann et al. have explored the 3D morphology of composite materials in Li-ion batteries [34]. David Stephenson in our group studied the ionic conductivity of Li-ion battery cathodes using the reverse Monte Carlo method [89].

The SG model in this work is built on concepts from the Reverse Monte Carlo (RMC) model, which differs from the standard Monte Carlo (MC) method. The MC Method uses
interaction potential to predict structure, while the RMC method iterates interaction potential to obtain the desired (experimental) structure. No input potential is required for RMC method. The RMC model is adjusted until the interaction probability agrees with experimental data [149].

6.2.1 Probability vs. Energy

The observed probability of a configuration is related to its relative free energy. The radial distribution function $g_{ij}$ is a normalized probability of pairwise interactions. The radial distribution function can be related to a so-called potential of mean force $w_{ij}$ as follows:

$$g_{ij}(r) = \exp \left[ \frac{-w_{ij}(r)}{k_B T} \right]$$  \hspace{1cm} (6.1)

where $k_B$ is Boltzmann’s constant and $T$ is temperature [149–151]. $g_{ij}(r)$ is obtained from a 2D image or 3D structure as shown in Chap. 5. The potential of mean force $w_{ij}(r)$ is a pairwise free energy, meaning it includes not only the direct pairwise potential energy ($E_{ij}$) but also the entropic energy due to other neighbors interacting with the original pair and forcing a change in configuration due to excluded volume. However, a classic MC algorithm uses direct pairwise interactions ($p_{ij}$) to generate model configurations, where $p_{ij}(r) = \exp \left[ -E_{ij}(r)/k_B T \right]$. Empirically, $g_{ij}(r)$ and $p_{ij}$ almost overlap at a short distance $r$, because $E_{ij}$ is large compared to the entropic terms also included in $w_{ij}(r)$.

In our SG model, the probability of FIB/SEM images (pairwise interactions $g_{ij}$) can only give the equivalent of potential of mean force $w_{ij}$, which is used as the initial guess for the direct pairwise potential energy $E_{ij}$ to generate model configurations. Because only lateral and diagonal nearest neighbor probabilities (considered to be a short distance) are utilized in the SG model, it is reasonable to use $g_{ij}$ as $p_{ij}$. In this way, as the model runs, $E_{ij}$ is iterated to improve agreement between $p_{ij}$ generated by the model and $g_{ij}$ generated by the experiment.
6.2.2 Previous Algorithms

This section summarizes the metropolis algorithm and periodic boundary conditions used in the previous SG model developed in our group.

**Metropolis Algorithm**  The Metropolis algorithm is a random walk method that accepts or rejects steps from one configuration to another in proportion to the relative probabilities of the two configurations [152, 153]. It aims to obtain approximate solutions to sampling or averaging problems with an extremely high number of degrees of freedom by focusing computation time on the most likely configurations. In this case, the acceptance or rejection of different configurations is key to generating samples that have the correct radial distribution function \( g_{ij} \). The Metropolis Algorithm is applied in this work as follows:

1. Start from an arbitrary configuration (random voxel distribution) with the same volume fraction as the experimental structures (ex. FIB/SEM images).

2. Randomly choose two sites \( s_I \) and \( s_J \) to swap; each proposed site must have at least one nearest neighbor of a different domain type. This reduces the anomalous formation of isolated domains occupying only one node.

3. Accept or reject each proposed move based on the transition probability function:

   \[
   P_{I \rightarrow J} = \min \left[ 1, \frac{P(x_n)}{P(x_o)} \right], \tag{6.2}
   \]

   where \( P(x_n)/P(x_o) \) is the relative probability of the two states \( (x_n \) is the new configuration and \( x_o \) the current configuration). If \( P(x_n)/P(x_o) > 1 \), then the new configuration is more probable than the old one and such a move is accepted. If \( P(x_n)/P(x_o) < 1 \), then the new configuration is less probable than the current state. Such unfavorable steps are accepted only if \( P_{I \rightarrow J} \) is greater than a pseudo-random number between [0, 1].
The relative probability of site $I$ containing domain $i$ is

$$G_i(s_I) = \prod_{s_k} p_{ik}$$

(6.3)

where a product is made for all $g_{ik}$ values between the central node $s_I$ and its nearest lateral and diagonal neighbors at sites $s_k$. The index $k$ indicates the domain identity of those neighbors. As mentioned above, each $p_{ik}$ value for a given pair type is precalculated from a FIB/SEM image at the same resolution as the SG model, but then is changed over the course of the simulation. The probability of a successful swap of domains $i$ and $j$, originally located on sites $s_I$ and $s_J$ respectively is based on Eq. 6.2, where the new configuration probabilities are $P(x_n) = G_j(s_I) G_i(s_J)$ and the old configuration probabilities are $P(x_o) = G_i(s_I) G_j(s_J)$.

**Periodic Boundary Conditions**  Periodic boundary conditions (PBC) are chosen for approximating a large (infinite) system by using a small part called a unit cell. PBC can be thought of as a replication of the simulation unit cell in all directions, like a solid crystal lattice. This allows the SG model to best reproduce bulk electrode structure from a minimum simulation volume. The SG model has the same resolution as the FIB/SEM structures. A standard personal computer can handle a cubic volume with an edge length of around 220 nodes; if the node size is 0.5 $\mu$m; this allows us to simulate a unit simulation box of dimensions $110 \times 110 \times 110$ $\mu$m to analyze transport properties. Here, 200 nodes per edge were used more typically for initial computations.

In addition, with PBC, the unit cell does not see a hard wall, but instead sees a copy of itself in all three dimensions. A hard wall would interrupt the bulk particle structure and lead to so-called edge effects. Moreover, it would be equivalent to an insulating or constant potential boundary condition and would therefore have a significant edge effect on the calculated effective transport properties.
6.3 Algorithm Improvement

This section describes the new algorithms developed as part of this work to improve the SG model for alkaline batteries. There is a tradeoff to adding more algorithms into the SG model. One of the advantages of the SG model is its simplicity compared to a particle dynamics type of model. Adding algorithms will necessarily increase the computer cost, thus causing us to lose the advantage of the SG model. However, more algorithms are desired to improve the microstructural description. In particular, the morphology of alkaline battery particles (EMD and graphite) is very different from the standard spherical morphology the SG model tends to generate. This work attempted to balance these two factors, producing a model with acceptable microstructure and conductivity while maintaining SG model algorithm simplicity at reasonable computation cost.

6.3.1 Input and Output

In order to increase SG model flexibility, the improved SG model not only reads real images but also image probabilities as inputs. In other words, a real image or cathode structure is no longer necessary. As long as the model is provided with specified probabilities, such as volume fraction and nearest neighbor probabilities, the SG model generates a configuration based on those input probabilities. This allows artificial changes in the probabilities to test the effect on the resulting predicted microstructure. For instance, the SG model can determine the level of change in both microstructure and transport properties as we alter volume fractions and nearest neighbor probabilities.

In addition, we also developed algorithms for outputting images for 3D configurations. 3D configurations have many advantages in visualization compared to 2D slices, which were used in previous work. Fig. 6.1 shows different 3D configuration displays, such as (a) volume display, (b) orthogonal display and (c) surface display.
6.3.2 Particle-Size Enforcement

One of the main efforts made to improve the microstructure description is through implementing particle size information into the SG model. The previous SG model generated a similar configuration in terms of particle sizes, regardless of differences in the input FIB/SEM images. For instance, the relative sizes of the carbon additives and active material are not adjustable in the previous SG model. In this work, one of our tasks is to better understand the characteristics of volume-efficient carbon additives. The carbon additives under investigation vary in size (6-85 µm). Thus, it is central to our SG model to distinguish carbon additive size.

This is done through occasional non-equilibrium moves that occur after a large number of Metropolis algorithm moves (as described in Sec. 6.2.2). Specifically, we swap or move two large blocks of voxels that have a spherical shape. These types of non-equilibrium moves are designed to form particles of a certain size, but on the other hand, they disturb thermodynamic equilibrium or act to stir the system, which in practice also leads to rearranging or breaking up equilibrium particles [7]. More details are discussed below. Swapping two spheres improves model structure without significantly disturbing or undoing other algorithms such as nearest neighbor probabilities.
**Elongated Graphite**  We observed that graphite particles in FIB/SEM images showed elongated features. One way to generate these long-range graphite features is to connect two carbon domain groups, as illustrated in Fig. 6.2. The algorithm steps are as follows.

1. Randomly find first carbon site.

2. Find a sphere containing more than 75% carbon. 75% is an empirical figure; a range from 70-80% is recommended to balance computation efficiency while avoiding an endless loop. The sphere diameter range is chosen from a uniform distribution with an average equal to half the experimental median carbon particle size. (Dash circle 1 in Fig. 6.2).

3. Randomly find second carbon site.
4. Accept second carbon site if the distance between the two sites is three times larger than their radius to avoid a trivial solution. Boundary condition is applied to calculate the two sites’ nearest distance.

5. Find a sphere containing more than 75% carbon. The sphere diameter is the same as the first carbon site sphere (dashed circle 2 in Fig. 6.2).

6. Determine the amount of other carbon inside each sphere, and calculate the effective radius of the carbon clusters found within each sphere (solid circle 1 and 2 in Fig. 6.2).

7. Find the center sites of the two carbon sphere in step 6, and document the position of the remaining carbon voxel in the spheres relative to the center site.

8. Compare the effective radii of the two carbon clusters.

9. Create sub-spheres next to the larger carbon cluster with the same radius as the small cluster (solid circle 3 in Fig. 6.2).

10. Swap the identity of the nodes in the smaller carbon cluster with the sub-spheres according to their relative position.

Using this algorithm we have succeeded in making elongated graphite particles within the SG model. As observed in Fig. 6.3, the carbon additives in (c,d) show long-range features compared to the model configuration from the previous model.

**Large EMD**

EMD has a large particle size distribution and often one or two large particles ($\geq 40 \mu m$) are observed in FIB/SEM images. However, in the previous SG model, carbon and pore domains were well dispersed; therefore, large active material (EMD) particles are rare. A simple move is added to increase the appearance of large EMD particles. The algorithm steps are as follows.

1. Randomly find first EMD site.
2. Find a sphere containing more than 75% EMD. 75% is an empirical figure; a range from 70-80% is recommended to balance computation efficiency while avoiding an endless loop. The sphere diameter range is chosen from a uniform distribution with an average equal to the experimental median EMD particle size.

3. Assign all the voxels within the sphere to EMD and keep track of the number of all non-EMD voxels (carbon and pore domain) replaced with EMD.

4. Randomly find EMD-carbon pairs and change the EMD voxel identity to carbon.

5. Repeat step 4 until all the carbon domains replaced in step 3 are placed along the EMD-carbon pair interface.

6. Randomly find EMD-pore pairs and change the EMD voxel identity to pore.

7. Repeat step 6 until all the pore domains replaced in step 3 are placed along the EMD-pore pair interface.

This algorithm succeeded in producing larger EMD particles. Steps 5 and 7 are done to conserve the number of voxels of each domain type and also to minimize disturbances to nearest neighbor probabilities. In addition, this algorithm increases the surface roughness of the carbon and pore domains. The final configuration is insensitive to the percentages used in the above algorithm, provided that the percentage falls within the recommended range.

Fig. 6.3 compares model configurations with (c,d) and without (a,b) applying the particle-size-enforcement algorithms described above. Parts (a) and (c) are sliced views, while parts (b) and (d) are 3D volume displays of the model configuration. Model configurations using particle-size-enforcement algorithms displayed better descriptions of EMD and carbon domain size. Unexpectedly, our effort to improve particle size description also had the benefit of modestly improving the domain shapes. This is due to the fact that non-equilibrium moves encourage irregular shapes rather than round particles.
6.3.3 Tip-Growth Move

Fig. 6.4 (a) shows a section of FIB/SEM image for the baseline cathode, where both graphite and pore domains have a high aspect ratio or needle-like features. Even though the model configuration (Fig. 6.4 (b)) after the particle-size-enforcement move displays improved domain size distribution and surface roughness, insufficient cracks or needle-like features are still observed in model configurations. A few trial moves were designed to augment such
features, but none of them are implemented in the SG model because those moves would yield only modest improvements while greatly increasing model complexity.

For completeness, we include here one of these moves, named the tip-growth move because it grows the tip and edges of the carbon and pore domains. The tip-growth algorithm shown below is our effort to implement n-point correlation (discussed in Chap. 5) into the SG model.

1. Define the domain tip as a voxel that has only one lateral neighbor of its own kind in one plane.

2. Calculate the probabilities of carbon and pore domains having a tip in the FIB/SEM images.

3. Normalize tip probabilities with a respective domain volume fraction called relative tip probability.

4. Compare the domain tip probabilities between model configurations (Psimtip) and FIB/SEM images (Ptip).
5. Pick a domain for tip for tip growth based on Step 4. For example, pore.

6. Find a pore tip by randomly picking plane xy, yz, xz and see if it contains a tip.

7. Find the neighbor (opposite position of tip-pair) identity.

8. Find another matching pair of sites (ex. EMD and pore interface).

9. Swap their identities to grow a tip.

10. Repeat steps 4 to 9 to improve the match between the simulation (Psintip) and image (Ptip).

The ineffectiveness of tip growth moves may be due to their interruption of particle-size enforcement moves. For example, the algorithm which creates large EMD particles is likely undo tip growth moves.

6.3.4 Termination

As configured, the previous SG model iteration was terminated when the squared error difference in the lateral $P_{ij}^L$ and diagonal $P_{ij}^D$ nearest neighbor probabilities between the model configuration and the image reached a minimum. At the same time, the metropolis algorithm tends to minimize the inter-facial area between particles, so the particles in the final configuration often looked like Fig. 6.3 (a), where particles appear as spheroidal features. However, the actual imaged system is a collection of meta-stable solid particles that do not necessarily exhibit a thermodynamic minimum energy, but rather a mechanical equilibrium.

In this work, the SG model trajectory was terminated using the same criterion as the previous SG model. However, one could potentially terminate the model trajectory at earlier steps to save the computation time, in the case where the final configuration was relatively insensitive to the the number of steps or iterations in terms of computed conductivity. Fig. 6.5 shows the model configuration terminated before and after the final configuration (around 380 million iterations). The effective electronic conductivities of configuration (a) and (b)
are 120.3 ± 44.9 S m\(^{-1}\) and 85.8 ± 30.7 S m\(^{-1}\), respectively. Note that the uncertainties are standard deviation for three independent directions. Then if do t test comparing two means, we can say they come from same population of the 85% confidence level.

6.4 Model Results and Discussion

One could use all the metrics developed in Chap. 5 to compare the SG model and our experimental results. Not all the metrics are used simultaneously for every material-to-material comparison below.

6.4.1 Model Validation

The SG model is validated in two ways. First, microstructures are compared between the model configuration and the 3D FIB/SEM structure of the baseline cathode. Second, transport properties are compared between the model configuration and experimental measurements.
Fig. 6.6 compares the SG model configuration with the 3D FIB/SEM structure. They differ in some aspects and resemble each other in others. The FIB/SEM structure shows a high-aspect ratio for the pore and carbon domains. At the same time, the SG model configuration displays the same volume fraction, as well as similar nearest neighbor properties and domain size distributions as the 3D FIB/SEM structure.

Figure 6.6: (a) Volume view of SG model configuration (100 × 100 × 100 µm), (b) volume view of 3D FIB/SEM structure (76.5 × 173.5 × 65 µm).

Note that it is extremely difficult for the SG model to generate a structure identical to the FIB/SEM structures without additional sophisticated moves, which would only be capable of generating the exact structure found in Fig. 6.6 (b). Several modifications were attempted, but this was the best that this framework could produce. Therefore, the SG model is only able to semi-quantitatively predict microstructure and transport properties for a variety of porous electrode compositions.

The effective conductivities of the model configuration in Fig. 6.6 (a) are 88.4 ± 19.2 S m⁻¹ for electronic conductivity and 2.63 ± 0.01 S m⁻¹ for ionic conductivity, compared
respectively to $138.8 \pm 43.8 \text{ S m}^{-1}$ and $2.65\pm 0.23 \text{ S m}^{-1}$, computed for the corresponding of FIB/SEM structure (Fig. 6.6 (b)). This indicates that a high aspect ratio of carbon domain is quite favorable to electrode effective electronic conductivity. In contrast, the high aspect ratio of the pore domain in the FIB/SEM structure does not make much difference in ionic conductivity, which suggests that ionic conductivity is less sensitive to pore domain morphology.

6.4.2 3D vs. 2D Input

Comparing SG model results generated separately using 2D and 3D FIB/SEM structures as inputs can help us determine their sensitivity to these inputs. One could use only a representative 2D structure instead of a 3D structure as the model input if the two structures generate similar results in terms of microstructure and conductivity, since some microstructural features are theoretically identical for 3D and 2D FIB/SEM structures [42, 154].

![Figure 6.7: (a) The SG model configuration (100×100×100 µm) taking a 2D FIB/SEM structure as input, (b) the SG model configuration (100×100×100 µm) taking a 3D FIB/SEM structure as input.](image)

Fig. 6.7 shows the volume view of the SG model configuration based on separate 2D and 3D FIB/SEM inputs. The two structures are similar in terms of domain size and
contact probability. In addition, the computed conductivity of configuration (a) is 105 ± 33.6 for electronic conductivity and 2.75 ± 0.03 for ionic conductivity, while configuration (b) electronic conductivity is 88.4 ± 19.2 S m\(^{-1}\) and ionic conductivity is 2.63 ± 0.01 S m\(^{-1}\). These two results are from the same population with a 65% confidence level. Thus the conductivity differences between the two SG model configurations are acceptable. Therefore, a representative 2D slice could substitute for a 3D structure as input for our SG model analysis.

6.4.3 BNB90 vs. MX15

For the purpose of investigating volume-efficient carbon additives for alkaline batteries, a variety of graphites were chosen and made into cathodes as shown in Sec. 4.3. Two other students in our group [102, 136] measured the electronic and ionic conductivity of those cathodes. In Chap. 7, correlations were presented between microstructure and transport properties. Here, some quantitative microstructure analysis are given for two cathodes compositions using the SG model.

Cathodes containing BNB90 and MX15 additives were used to test the SG model’s capability to distinguish carbon domain morphologies. BNB90 is an expanded graphite with a \(d_{90}\) around 85 \(\mu\)m, while MX15 is a non-expanded graphite with a \(d_{90}\) around 15 \(\mu\)m [155].

Fig. 6.8 compares structures generated by the SG model with cathode FIB/SEM structures. These model structures are comparable to experimental imaging structures in terms of EMD domain size. Also, the SG model structure of the BNB90 cathode (b) shows elongated features in the carbon and pore domains, which we observed in its FIB/SEM structure (a). Likewise, the SG model structure of an MX15 cathode (d) is similar to its FIB/SEM structure (c) showing a short-range and dispersed carbon domain.

Table. 6.1 compares the conductivity between model configuration and experimental values for BNB90 and MX15 cathodes. It is evident that the SG model could semi-quantitatively predict microstructure and conductivity for cathodes composed of different carbon additives.
Figure 6.8: Structural comparison between a segmented 2D FIB/SEM image and a slice of our model configuration: (a) 2D FIB/SEM ($233.5 \times 211 \mu m$) of baseline cathode, (b) SG model slice view of baseline cathode ($100 \times 100 \mu m$), (c) 2D FIB/SEM ($247.5 \times 280.5 \mu m$) of 5 wt% MX15 at 22.2% overall porosity, (d) SG model slice view of the MX15 cathode ($100 \times 100 \mu m$). (For FIB/SEM image: gray is EMD, black is carbon domain, and white is pore. For SG model structure: green is EMD, red is carbon domain, and blue is pore.)
Table 6.1: Conductivity comparison of model configuration and experimental values for BNB90 and MX15 cathodes.

<table>
<thead>
<tr>
<th>Effective conductivity</th>
<th>Electronic (S m(^{-1}))</th>
<th>Ionic (S m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Computation</td>
<td>Experiment</td>
</tr>
<tr>
<td>BNB90</td>
<td>105 ± 33.6</td>
<td>161</td>
</tr>
<tr>
<td>MX15</td>
<td>21.1 ± 2.5</td>
<td>40</td>
</tr>
</tbody>
</table>

6.4.4 BNB90 Fraction

BNB90 produces the highest conductivity of any of the carbon additives tested [102]. The SG model is used to predict transport properties for BNB90 cathodes of various mass fractions from 2 wt% to 6 wt%, which is within the range of desirable carbon additive composition [20, 156]. Fig. 6.9 shows the segmented FIB/SEM images for BNB90 cathodes. 5 wt% BNB90 cathodes are presented in Fig. 6.6 and 6.8. All the cathodes are prepared under the same conditions as described in Sec. 4.3. These cathode images are the inputs for the SG model.

Fig. 6.10 plots the domain volume fraction and overall porosity for BNB90 cathodes based on Fig. 6.9. Some observations can be made. First, the overall porosity of electrodes decreases as the BNB90 mass fraction increases. This suggests that BNB90 could act as a lubricant and enhance EMD particle packing. As shown in Fig. 6.9, less inter-porosity is observed in cathodes with a high mass percentage of BNB90. Second, the EMD volume fraction stays relatively constant as the BNB90 mass fraction changes, which implies battery capacity (m\(_{EMD}/\)volume) does not necessarily decrease due to changes in the BNB90 mass fraction. This may be because mechanical compression properties are improved as additional graphite (lubricant) is added. In this way, the pellets are more compacted, so the overall volume of the pellets would decrease and the battery capacity (m\(_{EMD}/\)volume) stays the same even though less EMD is added. Further evidence is shown in Fig. 6.9, where the volume fraction of BNB90 and inter-pores have an inverse relationship. Increasing the BNB90 volume fraction mainly reduces the volume fraction of inter-particle pores.
Figure 6.9: Segmented BNB90 cathodes: (a) 2 wt% BNB90, (b) 3 wt% BNB90, (c) 4 wt% BNB90, (d) 6 wt% BNB90. FIB/SEM images are above $250 \times 250 \mu m$. 
Figure 6.10: Domain volume fractions of pellets with different BNB90 weight percentages based on FIB/SEM images shown in Fig. 6.9; the lines between points are to guide the eye.

Fig. 6.11 compares the transport properties of various BNB90 weight percentages between the SG model and experimental values. In general, the SG model correctly predicts trends for both electronic and ionic conductivity. However, the SG model typically under-estimates electronic conductivity. This may be due to the lack of high-aspect ratio carbon features in the SG model configuration. This also could be because the experimental conductivity was measured in the compression direction (Y direction) while model conductivity is the average of all three directions. On the other hand, the ionic conductivities computed using the SG model did not present as steep a slope as those of experimental values. This may be because the ionic conductivity is calculated using the volume of macro pores, while the experimental ionic conductivity was measured using overall porosity. As shown in Fig. 6.10, macro porosity and total porosity displayed different slopes as BNB90 content increased.
6.5 Model Prediction

6.5.1 Morphology

For the purpose of predicting the potential effect of domain morphology on transport properties, the SG model was used to generate three cathode configurations of different domain shapes and sizes while holding volume fractions the same (baseline cathode), as shown in Fig. 6.12. Configuration (a) is a random SG model structure. Configuration (b) is an equilibrium structure where the SG model was terminated when the nearest neighbor probability error was less than 0.5. Therefore, the shape of the domain has a high level of sphericity. Configuration (c) shows elongated graphite and pore domains by implementing the non-equilibrium moves introduced in Sec. 6.3. The right side of Fig. 6.12 shows corresponding graphite and pore domain size distributions for the three configurations.
Figure 6.12: The left panel contains 2D slices (100×100 µm) of diverse domain morphologies generated by the SG model. The right panel is the corresponding domain size distributions of the 3D model configurations. (For reference: green is EMD, red is carbon, and blue is pore)
Table 6.2: Transport property comparison of the configurations found in Fig. 6.12

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Electronic conductivity S m$^{-1}$</th>
<th>Ionic conductivity S m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3.15±0.04</td>
<td>2.32±0.01</td>
</tr>
<tr>
<td>(b)</td>
<td>3.95±0.26</td>
<td>2.36±0.01</td>
</tr>
<tr>
<td>(c)</td>
<td>67.95±14.77</td>
<td>2.65±0.13</td>
</tr>
</tbody>
</table>

Table 6.2 compares the transport properties of the three SG model configurations in Fig. 6.12. The random and equilibrium structures show similar electronic and ionic conductivities. However, configuration (c) exhibits notably higher electronic and ionic conductivity. The electronic conductivity of configuration (c) is more than 15 times higher than that of configuration (b). This indicates that domain morphology could significantly influence effective transport properties, especially electronic conductivity. In reality, configuration (b) could be considered non-expanded spheroid graphite while configuration (c) could be considered expanded graphite. The qualitative conductivity analysis of these electrodes is shown in Chap. 7.

Additionally, the configuration (b), similar to the previous SG model structure, was generated by the SG model when the difference between the nearest neighbor probabilities of the model configuration and image data was at its lowest point. The corresponding conductivity is far less than what was expected from experimental values. This suggests that nearest neighbor probability is not a sufficient metric to describe alkaline battery microstructure.

### 6.5.2 Cell-Level Simulation

Chap. 5 and 6 discussed how effective conductivity changes with domain conductivity and cathode microstructure, such as graphite type, graphite fraction, and domain morphology. Up to this point, a few important questions to ask have included: how do these changes in structure affect overall cell discharge performance? What potential improvement in cell performance could be done through manipulating microstructure? These questions were answered using a combination of our microstructure model and a 1D-Newman type model.
for alkaline batteries. The 1D-Newman type model is proprietary and was provided by InTae Bae [157]. The parameters of the 1D-Newman model can be found in a series of publications by the Cheh group at Columbia University [158–163].

Fig. 6.13 shows an alkaline battery cell performance curve for various cathode effective electronic conductivities at (a) 1A and (b) 0.25 A discharging rates. 1A discharge represents a high-rate application. 0.25A discharge represents a normal-rate application. The cathode effective electronic conductivity was varied from 3 to 150 S m$^{-1}$. Dropping electronic conductivity from 150 to 10 S m$^{-1}$ during discharge would have little effect except at very large currents (high-drain performance). By comparing these results to the conductivity results from Fig. 6.11, we conclude that cathodes of BNB90 mass fraction 3-4 wt% are recommended for normal-rate applications where cathodes of higher BNB90 mass fractions would not yield further benefits. On the other hand, alkaline batteries for high-drain performance are more sensitive to electronic conductivity changes (Fig. 6.13 (a)). Thus, highly effective electronic conductivity is preferable (above 150 S m$^{-1}$ or 5 wt% BNB90) for reliable performance with such a cell. It is worth mentioning that the electronic conductivity in Fig. 6.11 is dry cathode conductivity, while the introduction of an electrolyte (8.7 M KOH) into dry cathodes reduces the electronic conductivity of dry cathodes by around a factor of 3 [9].

Fig. 6.14 presents cell discharge curves for various ionic cathode conductivities. Decreasing ion transport has a large effect on cells, even at normal discharge rates. Combining Figs. 6.11, 6.13 and 6.14, we conclude that 3 wt% is the pivotal BNB90 graphite mass fraction for superior cell performance at a normal discharge-rate. The effective electronic (wet) and ionic conductivity for the 3 wt% BNB90 cathode in electrolyte would be around 10 and 4 S m$^{-1}$. Further decreasing the BNB90 mass fraction results in a rapid drop in electronic conductivity, hurting overall cell performance. At the same time, further increasing the BNB90 mass fraction to 5 wt% would likely reduce ionic conductivity to 2.5 S m$^{-1}$, leading to poor cell performance as shown in Fig. 6.14. Moreover, one could increase the
Figure 6.13: Alkaline battery discharge performance at (a) 1A and (b) 0.25 A discharging rates of various cathode electronic conductivities.
intra-particle porosity of EMD to enhance cathode ionic conductivity toward $8 \text{ S m}^{-1}$ for a flatter discharge curve.

6.6 Conclusion

The SG model is an analytical tool used to generate microstructures and calculating their macroscopic transport properties. New algorithms were developed to better describe simulated geometric cathode microstructure. Swapping two spherical regions of multiple voxels was found to be effective at improving model structure without significantly disturbing key metric algorithms such as nearest neighbor probability. The improved SG model results are mostly validated with experimental microstructures and transport properties.

The SG model allows us to predict trends in cathode performance for diverse carbon types and fractions. The SG model results are compared to experiments for BNB90 and MX15 cathodes, as well as various BNB90 weight percentage cathodes, and the modeled transport properties semi-quantitatively agree with the experimental values. In addition, it is found that a representative 2D slice could substitute for a 3D structure as input for the SG model.
Domain morphology significantly influences effective transport properties. Electronic conductivity is especially sensitive to moderate changes in structure. Additionally, dropping effective electronic conductivity from 150 to 10 S m$^{-1}$ during discharge would have little effect on cell performance except at large currents (high-drain performance). Decreasing ion transport, however, has a large effect, even on cells operating at normal discharge rates.
Chapter 7
Correlating Microstructure To Conductivity

7.1 Introduction

This chapter continues to analyze the relationships between materials, microstructure, and performance for primary alkaline battery cathodes. The SG model predicted certain characteristics of selected materials for volumetrically efficient conductive additives. This chapter correlates microstructure to cathode conductivity (high or low) of various carbon additives. FIB/SEM microstructures are used to characterize the cathode’s overall microstructure. Most of the analysis here is qualitative and is performed by examining images and looking for characteristics which contribute to conductivity difference. Parts of this chapter were published in Ref. [9].

7.2 Measurements of Conductivity

Carbon additives are necessary for passing electrons, but they also influence electrolyte transport in the cathode. They play a pivotal role in the overall conductivity of the cathode.

Two types of carbon additives are investigated: carbon fiber and graphite. Carbon fibers are reported to provide excellent bulk or long-range conductivity due to their high aspect ratio [61, 137, 164–166]. However, they are used less often because of cost, mixing difficulty and their potential to cause an electrical short across the separator [167, 168].
Graphite has a relatively smaller aspect ratio compared to carbon fiber, yet it is commonly used in commercial alkaline batteries because it has good conductivity and is inexpensive [134, 138]. The carbon additives used in this work are the same as those used for our conductivity measurements, including TIMCAL graphite (MX15, KS15, KS6, SFG6 and BNB90) [155], graphene (graphene nanopowder)[169], and nanofiber (pyrograf nanofibers) [170]. Characteristic physical properties for each of the investigated carbon additives are shown in FIB/SEM images in this chapter, and additional details are summarized in Ref. [9].

Electronic and ionic conductivity were measured separately by two students in our group using different apparatuses [102, 136]. Both efforts quantify the relationship between conductivity and porosity for all the carbon additives. Doug Nevers used a two-point probe apparatus to measure the electronic conductivity for 5 wt% carbon additive cathodes. Mehdi Forouzan measured ionic conductivity for cathodes of 4.3 wt% carbon additives and varied the BNB90 mass fraction. SFG 6 and nano-fiber carbon additives are not included in the ionic conductivity experiment because of difficulty in making the pellets, as explained in Ref. [136]. To sum up their results, high porosity increases ionic conductivity but decreases electronic conductivity. In addition, a similar inverse pattern is true for different carbon additives. The carbon additive that presented the highest electronic conductivity also had the lowest ionic conductivity.

Fig. 7.1 shows the electronic (a) and ionic (b) conductivities of each measured carbon additive cathode at an overall porosity of about 27 %, which is similar to that of a commercial battery cathode [144]. Comparing parts (a) and (b), we first note that electronic conductivity is at least one magnitude greater than ionic conductivity. Here, electronic conductivity was measured at 5 wt% and ionic conductivity at 4.3 wt%. Similar to the Li-ion battery discussed in Chap. 3, this shows that ionic transport is likely the limiting factor in overall transport properties. Second, carbon additives affect ionic and electronic conductivity differently. BNB90 and graphene are the outstanding performers in electronic conductivity.
measurements; in contrast, the two carbon additives display slightly inferior ionic conductivity compared to the rest of the carbon additives. Third, the rest of the carbon additives, despite having a range of physical properties, produced similar electronic \((27 \pm 4.7 \text{ S m}^{-1})\) and ionic conductivities \((4.9 \pm 0.6 \text{ S m}^{-1})\).

### 7.3 Measurements of Microstructures

This section shows microstructures and then correlates the microstructures and conductivities for the different carbon types. The additives under investigation can be divided into three categories: expanded graphite (BNB90 and graphene), fiber mixture, and non-expanded graphite (MX15, KS15, KS6 and SFG6). FIB/SEM is used to characterize the cathodes’ overall microstructure. Cathodes for imaging are made of 4.3 wt% carbon additives, and the fabrication process is described in Chap. 4. Fig. 7.2 shows the overall porosity of different carbon additive cathodes (54 psi), which are used for FIB/SEM imaging. The 90 wt% MX15/10 wt% fiber has the highest overall porosity. KS6 has the lowest overall porosity.
7.3.1 Expanded Graphite

BNB90 and low-cost graphene perform notably better in electronic conductivity measurements, and both carbon additives can be considered expanded graphite, made of partially separated graphene layers. Within graphene layers, carbon atoms are bonded with resonant covalent bonds which result in good electrical conductivity. Fig. 7.3 presents (a, c) BNB90 and (b, d) graphene cathodes. The aggregation of carbon additives crosses both the milled cross section and cathode surface. The milling depth is around 5 micrometers. According to the manufacture’s material data sheet, the D90 values for BNB90 and graphene are 85 and 4.5 µm, respectively [155, 169]. However, BNB90 and graphene in Fig. 7.3 show a long range, continuous carbon network (more than 150 µm). Thus, the long-range connectivity of carbon domains in addition to high conductivity within graphene layers are likely the main reason for the outstanding electronic conductivity of expanded graphite.

In addition, BNB90 and graphene cathodes show relatively low ionic conductivity. According to Fig. 7.2, they actually have a higher overall porosity compared to the other carbon additive cathodes, which are prepared under the same conditions (pressure). In other words,
Figure 7.3: FIB/SEM images for (a, c) BNB90 and (b, d) graphene based cathodes. (For reference: the gray is EMD, the black is carbon, and the pores appear a dark gray.).

the fact that expanded graphite as a carbon additive shows low ionic conductivity is not due to inferior or lower overall porosity, instead, it is may because expanded graphite increases the higher-level complexity of tortuosity in contrast to other carbon additives.

Parts (c) and (d) of Fig. 7.3 show an overall view of a BNB90 and a graphene cathode, respectively. These images show carbon domain abundant and deficient regions in the 100 µm² scale, with the carbon domain deficient regions marked with a red box. Fig. 7.4 (a) is a magnified carbon-additive-abundant region of a BNB90 cathode, showing intimate contact between expanded graphite and EMD. Fig. 7.4 (b) is a close-up of a carbon-additive-deficient
region of a BNB90 cathode, exhibiting a large volume of inter-particle pores. This could explain why expanded graphite cathodes display higher overall porosity. BNB90 and graphene are aggregated into a long-range carbon domain, which leads to a large carbon-deficient region of greater porosity.

7.3.2 Non-expanded Graphite

Fig. 7.5 shows a cross section of the four carbon additive cathodes: (a) MX15, (b) KS15, (c) KS6 and (d) SFG6. The four carbon additives are all Timcal graphites of different particle sizes and shapes [155]. For example, the number 15 in type KS15 means that the $D_{90}$ value is around 15 $\mu$m and the KS indicates that the shape of the graphite is isometric and irregular spheroids. On the other hand, MX and SFG mean that the graphite particles are anisometric flakes. The rest of the graphite samples follow the same logic. Again, these carbon additives, despite having a range of physical properties, produced similar electronic ($27 \pm 4.7$ S m$^{-1}$) and ionic conductivities ($4.9 \pm 0.6$ S m$^{-1}$) [9, 136].

According to Fig. 7.1, spherical graphite cathodes have a slightly higher ionic conductivity compared to all other flake graphite cathodes. Comparing images in Fig. 7.5, spherical graphite cathodes (b) and (d) do not exhibit a higher level of inter-particle porosity. Adding
Flake carbon additives may increase the tortuosity of the cathode's carbon domain regions due to the large amount of nano pores in flake graphite, as shown in Fig. 7.6. This is despite the fact that there is a modestly larger amount of inter-particle pores in flake-type carbon additives, especially for the graphene cathodes (Fig. 7.6 (a)).

Fig. 7.6 (b) is an example of spherical graphite cathodes made of KS15, which shows the highest overall ionic conductivity for cathodes of the same graphite mass fraction. The KS15 carbon domain in the cathode (Fig. 7.6 (b)) appears to show a smaller amount of inter-particle pores in the carbon domain than does graphene (Fig. 7.6 (a)).
Figure 7.6: FIB/SEM images of flake carbon additive (a) graphene and spherical carbon additive (b) KS15 cathodes.

Furthermore, all graphites may serve not just as a conductivity additive but also as a lubricant during the compression process, thus enhancing compression and binding with EMD during manufacturing. As shown in Fig. 7.4 and 7.5, Graphite and EMD have intimate connections than EMD particles themselves. In Fig. 7.5, the smaller carbon-additive particles (c,d) appear to be more dispersed between the EMD particles. In other words, EMD particles are more likely to be surrounded by carbon additives and carbon-deficient regions are rarely observed.

### 7.3.3 Fiber Mixture

Both the local particle-to-particle contacts and the long-range connectivity of the carbon domains are important to overall electronic conductivity performance. For the purpose of enhancing the long-range connection for non-expanded graphites such as MX15, nanofibers (pyrograf nanofibers [170]) were mixed into MX15 as a new carbon additive. Fig. 7.7 shows FIB/SEM images of the 50/50 wt% MX15/nanofiber (total 4.3 wt%) cathode. As shown in parts (a) and (b), the pellets cannot hold together after pressure is released and present large gaps. This may be due to poor nanofiber binding or the elastic properties of nanofibers...
compared to graphite carbon additives. The nanofibers are not able to deform permanently like the graphite additives. Parts (c) and (d) are a closer view of the nanofiber or MX15/nanofiber mixture. Nanofibers tend to create vacancies between themselves, leading to larger bulk volume.

To correct this observed problem, a smaller fraction of nanofiber (10 wt% instead 50 wt%) in the carbon mix was used to form a pellet. However, it was found that the addition of a small fraction of fibers (10/90 wt% nanofiber/MX15 mixture) does not significantly change the electronic conductivity relative to the MX15-based cathodes. Fig. 7.8 (a) is the cross

Figure 7.7: FIB/SEM images for 50 wt% MX15/50 wt% nanofiber cathode: (a) side view of the pellet, (b) cross section of the cathode, (c) surface view of nanofiber, (d) surface view of MX15 and nanofiber mixture.
section of a 10/90 wt% nanofiber/MX15 mixture cathode, and the fibers are not obvious in the cross section, partially because the nanofiber has a diameter of only 150 nm. There is not a compelling difference observed between the fiber mixture (a) and MX15 (b) cross sections. Parts (c) and (d) more closely examine the nanofiber mixture and EMD region. The connections observed within the nanofiber mixture are not as as close as the graphite connections from Fig. 7.6 and 7.5. Thus, even though nanofibers have good long-range (50-200 µm) conductivity, cathode effective electronic conductivity is low because the nanofibers lack close connections with other nanofibers, graphite (MX15) or EMD particles. Therefore, suitable carbon additive candidates for alkaline batteries have not only superior long-range electronic conductivity and low tortuosity, but also are easily deformable by the surrounding EMD particles.

In summary, a more continuous and aggregated carbon domain provides better long range connections for electronic conductivity. Small, non-expanded carbon additives not only enhance local carbon connections, but also improve ionic conductivity. This suggests that a combination of expanded graphite with non-expanded graphite (MX15, KS15, KS6 and SFG6) could be a solution to balancing electronic and ionic conductivity in alkaline batteries. Moreover, non-expanded graphites are much less expensive than graphene or BNB90.

7.4 Wet Cathodes

Concentrated KOH solution is added into the annular cathode pellet as the electrolyte for alkaline batteries [171]. Some experiments were done to understand electrolyte effects on transport properties. We found the electronic conductivity of expanded graphite cathodes with concentrated KOH decreased by about 30% relative to that of the dry cathodes [9]. BNB90 cathodes were used to observe microstructural changes when electrolyte is introduced into the cathode. The environmental scanning electron microscope (ESEM) collects images
Figure 7.8: (a) Cross section of 90 wt% MX15/10 wt% nanofiber mixture cathode, (b) cross section of MX15 cathode, parts (c) and (d) are closer views of the 90 wt% MX15/10 wt% nanofiber mixture cathode of specimens that are wet and allows for a gaseous environment in the specimen chamber. ESEM are applied mainly in biology to image specimens in their natural state.

The original purpose of doing ESEM is to view changes in cathode microstructure during the wetting process. Fig. 7.9 shows the BNB90 cathode imaged at different chamber moisture levels. Part (a) is a cross section before adding 8.7 M of KOH electrolyte, Part (b) is the BNB90 cathode at 80% moisture content (5 Torr, 4°C), where the wet cathode is covered by electrolyte. Part (c) is the BNB90 cathode at 17.5% moisture content (1.1 torr, 4°C), where
Figure 7.9: FIB/SEM images of BNB90 (4.3 wt%) cathode: (a) dry cathode without electrolyte, (b) cathode at 5 Torr after 8.7 M KOH electrolyte was added, (c) cathode at 1.1 Torr after 8.7 M of KOH electrolyte was added.

most of the electrolyte has dried out and left only layer of salt behind. This experiment failed to fulfill the purpose due to the cathode being hidden under electrolyte or salt.

There are a few possible solutions to the above issue. One could mill off the KOH salt deposition layer to view the cathode microstructure. The downsides of this method are that the region is too large to mill and there is a possibility of over-milling the cathode. Another method is to use deionized water instead of the concentrated KOH solution; however, according to a previous study, adding deionized water affects electronic conductivity differently.
Figure 7.10: (a) surface of dried out cathode of off shelf alkaline battery, (b) fresh cross section view of commercial cathode, (c) element EDAX analysis of cathode surface (a), (d) is the EDAX of region 1, (e) is the EDAX of region 2, (f) is the EDAX of region 3.
Figure 7.11: FIB/SEM image of alkaline battery cathode: (a) dry cathode, (b) dried out commercial cathode.

than KOH [9]. A third way is to compare the dry cathode to the cross section of a commercial alkaline battery cathode. This third method is used in this work. The commercial battery cathodes are meant to be representative.

Fig. 7.10 shows the microstructure and corresponding EDAX analysis for a dried-out commercial alkaline battery. Part (a) is the surface of the dried out cathode covered by KOH salt, which appears to be similar to that found in Fig. 7.9 (d). The corresponding EDAX analysis is shown in (c), showing evidence of potassium. Thus, the deposited material is most likely KOH salt. Part (b) is the cross section of a commercial cathode with three regions marked with red boxes. Region 1 is the carbon domain region with the EDAX evident in (d). Region 2 is the EMD region with the EDAX evident in (e). Region 3 is a mixture of EMD/carbon/KOH, and the most potassium-rich region compared to the carbon and EMD region, indicating the porous EMD/carbon region in Fig. 7.9 (b) is most accessible to the KOH solution.

Fig. 7.11 compares the microstructure of (a) dry cathode (no electrolyte) and (b) dried-out commercial cathode. Both images are marked with three regions for convenience in comparison. Again, region 1 is the carbon/domain, region 2 is a pure EMD region and
region 3 is the porous EMD/carbon region. The region with the most noticeable changes is region 3, where particles were likely rearranged during the KOH intrusion. This modification could increase the particle-to-particle contact resistance, decreasing the ability of electrons to tunnel through the associated interfaces [40, 172].

7.5 Conclusion

This chapter correlates microstructure to the conductivities of different alkaline battery cathodes fabricated with different carbon additives. Expanded graphites exhibited well-connected and elongated carbon pathways in SEM/FIB cross sections, which most likely contributed to their high electronic conductivity performance. However, expanded graphites additives display slightly inferior ionic conductivity. Adding expanded graphites may increase ion transport difficulty by increasing cathode tortuosity in the carbon domain. A large amount of inter-particle pores are observed in the electrode with the graphene carbon additive. The rest of the investigated non-expanded carbon additives, despite having a range of physical properties, produced similar transport properties. Additionally, KOH solution likely impairs cathode electronic conductivity by modifying the particle-to-particle interfacial area, especially the porous EMD/carbon region.

All graphites may serve not just as a conductivity additive but also as a lubricant during the compression process, thus enhancing compression and binding with EMD during manufacturing. The nanofiber material under investigation lacks compressibility and thus is not a suitable carbon additive candidate for alkaline batteries.
Chapter 8
Summary and Scope of Future Work

8.1 Summary of Results

A combination of experiments and models was used to understand how microstructure affects the transport properties of porous electrodes. First, the electronic conductivity of porous cathodes was directly measured with our four-line probe. Second, imaging techniques were developed to obtain experimental 3D cathode microstructures. Third, additional metrics were explored to characterize the microstructures. Fourth, the stochastic grid model was used for Li-ion batteries previously and here was improved and adapted for alkaline batteries. Finally, qualitative analyses were made to correlate microstructure to conductivity for cathodes with a wide range of carbon additives. This work provides an improved experimental understanding of the connection between microstructure and cell performance.

This work investigated two commonly used battery systems: Li-ion and alkaline batteries. Both battery cathodes are treated as three-domain heterogeneous systems composed of active material (A), carbon additives (C) and macro-pore (P) regions. Not all the above tasks were applied to both battery systems in this work because of collaboration with other colleagues and the research needs of our group. The following paragraphs highlight lessons learned or techniques developed in this work. A more detailed summary can be found at the end of each chapter.

Ionic conductivity is the limiting transport mechanism for pristine (uncycled) cathodes. This is true for both Li-ion and alkaline batteries. Direct conductivity measurements were
designed for both electronic and ionic properties. In this work (Chap. 3), a four-line probe was used to quantify electronic conductivities for LiCoO$_2$ cathodes. Electronic conductivity was increased by reducing the cathode porosity and raising the carbon domain fraction. The presence of electrolyte reduced electronic conductivity to around 0.4 times the dry value for LiCoO$_2$ cathodes. Combining this work with other works on conductivity measurements [9, 53, 136], we see that the wet electronic conductivity of the baseline LiCoO$_2$ cathode is around 80 times greater than the ionic conductivity for a porosity of 35%, and the wet electronic conductivity of the baseline alkaline cathode is around 40 times greater than the ionic conductivity for a porosity of 24%.

Protocols and techniques for acquiring, processing and segmenting series of FIB/SEM images were developed in this work (Chap. 4). These images are generally larger than typical 3D FIB/SEM structures obtained in other reported studies and represent a substantial amount of work. Many image segmenting methods were attempted, namely manual segmentation, computer auto segmentation, human-assisted computer segmentation and hybrid segmentation. The preferred solution for segmenting a series of images for our most-investigated system, alkaline cathodes, is hybrid segmentation, which is done by using a computer algorithm to segment the image into active material and pore phases, then identifying carbon phases manually.

Four metrics, namely, domain size distribution, aspect ratio, volume-metric surface area $\alpha$ and Fourier transform coefficient, were developed to describe electrode microstructure. Those four metrics, in addition to volume fraction and nearest neighbor probabilities, are compared between non-imaging methods, 2D FIB/SEM, 3D FIB/SEM, and 3D X-ray microstructure. There is reasonable agreement between the different methods in terms of volume fraction, while other metrics vary. Additionally, a new method was developed to approximate domain conductivity. One can use a reconstructed 3D microstructure (FIB/SEM) and experimental effective conductivity to approximate the domain conductivity using a 3D structure conductivity computation algorithm developed in this work (Chap. 5).
The previous stochastic grid (SG) model has been adapted and developed to predict the microstructure and transport properties of alkaline batteries. The 3D model configuration was created using the interactions between different domains described in terms of probabilities. The previous SG model produced a particle structure that was too smooth or rounded, regardless of input particle morphology. The cause of this was identified as thermal equilibrium. We corrected this thermal equilibrium feature and partially matched the particle morphology in the simulation with the raw material morphology. Preliminary SG model results are presented for microstructure changes with respect to graphite fractions and particle morphology (Chap. 6).

A new perspective on correlating microstructure to conductivity in alkaline battery cathodes is presented in Chap. 7. Expanded graphite exhibited well-connected and elongated carbon pathways in SEM/FIB cross sections, which most likely contributes to their high electronic conductivity performance. However, expanded graphite additives display slightly inferior ionic conductivity. This decrease in effective ionic conductivity is likely due to very large tortuosity in the expanded graphite carbon domains. A relatively large amount of inter-particle pores are observed in the graphene carbon additive.

8.2 Future Work

Some potential future modeling and experimental work is indicated below. The discussion reflects the view that a combination of modeling and experiments is a preferable approach to investigate microstructure’s effect on transport properties. A model reflects our understanding of our experiment and allows for rapid hypothesis testing. Further, a model can predict microstructure that is difficult to estimate through experiments. Experiments most effectively evaluate model selection and capability.
8.2.1 Model

Good electronic and ionic conductivity are both necessary for better battery performance, but are not sufficient conditions. Potential changes in cell performance due to microstructure changes are not validated experimentally. Only some modeling results were given in Chap. 6, where we incorporate the SG model’s effective electronic and ionic results into a 1D Newman-type model to determine changes in overall cell discharge performance. This 1D Newman-type model assumes the microstructure only impacts conductivity without impacting other cell features. Experimental verification of cell performance is strongly recommended before using our modeling results in practice.

One can adapt the current SG model to fields beyond battery porous electrodes, such as petrophysics, reservoir engineering, mineral processing systems and porous structures in general [47, 75, 96, 146]. The SG model is simple, yet can qualitatively or semi-quantitatively predict multiphase porous media and structural properties such as permeability and tortuosity.

Adding additional metrics into the current SG model for a higher level of model accuracy is not recommended. The SG model is intended to be easily implemented. Additional metrics would result in a model that is too customized or particular to a specific system.

8.2.2 Experiment

Significant efforts were made to fabricate the Li-ion battery cathode as presented in Chap. 3 and Appendix A. Slurry viscosity was found to be crucial in successful cathode fabrication, yet a corresponding quantitative analysis has not been attempted. In addition, the yields of fabrication are low and vary by casting even though the same procedure is followed, which indicates that cathodes are sensitive to the fabrication process. A further investigation of cathode fabrication mechanics and key factors determining cathode yield would be a significant contribution to battery academia as well as manufacturers. One could develop a
cathode formation model to simulate the steps for making electrodes, and could also monitor physical properties during casting to identify components which lead to high cathode yields.

Electrode conductivity was measured only in the uncycled state, and ionic conductivity was found to be the limiting factor. In order to optimize microstructure in terms of conductivity, examining electrode conductivity as a function of the state of charge would be valuable. An optimized structure would be able to function its best throughout its lifetime.

Multiphase image segmentation is not an easy task. One could use advanced image-acquiring techniques to reduce difficulties in image segmentation, and some preliminary results are shown in Chap. 4.
Bibliography


M. Rouse, what is aspect ratio (2005).

H. Wadell, Volume, Shape and Roundness of Quartz Particles (1935).


C. Van Loan, Computational frameworks for the fast Fourier transform, vol. 10 (Siam, 1992).


Appendix A

Manual for Li-ion Battery Cathode Fabrication

The purpose of this appendix is to help researchers successfully making Li-ion battery cathodes. The components of Li-ion battery cathodes are found in Table 3.1, and the fabrication steps are as follows:

1. Clean all the tools including the beaker, spatula, and scale, with isopropanol, and as needed, chem wipes.

2. Calculate mass for each component based on required loading according to Table A.1; the optimum NMP to dry basis is 36% for Composition 1 of Table 3.1.

3. Weigh out NMP and PVDF in the same beaker accurately to three decimal places and cover with aluminum foil (to prevent excess evaporation of NMP).

4. Dissolve PVDF in NMP using mild heat (around 80°C) for 20 minutes.

5. Weigh active material and carbon black in measurement tray (weight boat) and pour into mortar. Mix with pestle for 15 minutes.

6. Add the material from step 3 to the solution from step 2 (not the opposite), and mix the resulting slurry with an ultrasonic homogenizer for 15 minutes until well mixed.

7. Cut a 12 × 13 cm square of aluminum foil and roll it flat with a glass roller onto a piece of optically flat glass. Spray isopropanol onto the optically flat glass before placing the
aluminum on the glass. Make sure there aren’t any air bubbles between the glass and the aluminum.

8. Rapidly remove the slurry from the beaker with a spatula. Do not add the leftover material from the beaker to the aluminum in the spreading process which follows, since drying may have occurred and uniformity is the most important factor for the cast.

9. Spread the slurry using the doctor blade, which should be set to a higher number and reduced by increments of 20 µm. When it gets closer to the final thickness, reduce by small thickness increments such as 5 µm. Multiple passes over the slurry from different directions are recommended for a smooth surface and uniform thickness.

10. Let the film dry in air at room temperature overnight, which reduces the initial cast porosity by 5-10%.

11. Complete the drying in a vacuum oven at 100°C and a 22 mm Hg vacuum. Place metal bars on top of the uncoated aluminum to prevent the cast from curling up.

Figure A.1: Li-ion cathode fabrication spreadsheet.
Porosity Measurement and Calculation:

1. Cut $22 \times 30$ mm films from smooth areas in the center of the cast using a plastic template and a razor. Avoid the edges because the thickness is less uniform there.

2. Weigh out the mass of the film with a balance.

3. Measure the thickness of the film with a digital micrometer in nine separate locations.

4. The formula for porosity is $\varepsilon = \left( V_t - \sum \frac{m_i}{\rho_i} \right) / V_t$, where $V_t = h S$. $V_t$ is the total volume of cathode film, and $S$ and $h$ are the cross section and thickness of cathode, respectively. $m_i$ and $\rho_i$ are the mass and solid density of the cathode materials. Refer to Table 3.1 for components densities.

5. Use isopropanol to clean the rollers of the calendering machine in which the cathodes will be compressed to desired porosity. Decrease the gap slowly and roll the cathode through, then check with a micrometer, and narrow it down to the desired thickness.

6. Record the final weight of the material as well as the average thickness, porosity and loading of the battery.

Gallium Delamination of Aluminum Current Collector

1. Heat gallium on the hot plate and rinse with water. Used gallium is solid because of impurities and gallium is recycled to reduce expenses.

2. Place the cathode film on a paper towel, electrode side up, and spray with adhesive, then attach it to a $22 \times 30$ mm microscope cover glass.

3. Place the above sample on a larger and thicker glass slide for support, aluminum side up, and place on a hot plate with heat on low (temperature around 80°C).

4. Cover aluminum with liquid gallium and keep temperature at the same setting for 3-5 hours to allow the aluminum to dissolve in the gallium.
5. Heat a beaker of water to between 55 and 80°C.

6. Invert a small petri dish (bottom side up) inside of a larger petri dish (to catch the gallium and water runoff) as shown in Fig. A.2.

7. Put the larger glass slide onto the small petri dish, and make sure to place a couple of razor blades or some other flat object under the petri dish so as to keep the slide at a slight angle.

8. Use a plastic syringe to squirt water onto the molten gallium. The gallium should begin reacting and eventually roll off the slide.

9. Use two paintbrushes to carefully wipe off most of the excess gallium.
10. Add five drops of 1M HCl to the cathode and let it sit for a few minutes, and then rinse it off with water.

11. Slide a razor blade between the smaller and larger glass slides and lift the smaller slide onto a kimwipe for drying. Leave to dry for several hours.
Appendix B

Tutorial for Taking Series of FIB/SEM Images

This tutorial is to help researchers taking series of FIB/SEM images using Helios (FEI Helios Nanolab 600). Instrument information: resolution for electron beam and ion beam is 2 nm and 1.2 nm, respectively. Fig. B.1 is the Helios Nanolab 600 operating interface. Basic FIB/SEM operations can be learned through BYU’s microscopy lab training.

Figure B.1: Interface of the Helios Nanolab 600.
Get Started

1. Prepare the sample and mount it on the stub.

2. Vent the chamber, place the mounted sample in the stage, and make sure the sample heights are between the minimum and maximum marks on the reference gauge.

3. Pump the chamber until the microscope icon in the bottom right of Fig. B.1 turns green.

4. Wake up the electron beam, focus the sample and move the sample to the point of interest.

Adjust to Eucentric Height.

1. Select the electron window and adjust the focus to between 2500—5000x magnification, then link WD and Z.

2. Adjust Z to 4.2 mm under the navigation panel.

3. Refocus at high magnification and relink WD and Z.

4. Turn the magnification back down to 2500-5000x, and find an easily recognizable feature on the specimen as a reference spot.

5. Tilt the sample at 5 degrees, then center the reference spot in the SEM window by dragging points in the CCT (push the mouse wheel and drag it up and down, or double click that spot).

6. Tilt back to 0 degrees and recheck the reference spot.

7. Increase the tilt angle by small increments (5-20 degrees) until the sample is tilted at 52 degrees. Repeat steps 5 and 6 after each incremental movement.
8. Activate the ion beam and adjust it so its magnification is the same as that of the e-beam window, and drag the reference spot to the center of the screen (shift+left mouse drag). The sample is now at eucentric height.

**Set Up Slice and View Software**

1. Start Slice and View under the Windows Start menu, and hit the “create project” button.

2. Adjust the ion window magnification until the ion beam HFW is within 10 µm to 150 µm, as illustrated in Fig. B.2 (a). This limits the width of the images in the series to around 90 µm when the HFW is adjusted to 128 µm.

3. Set up image resolutions and dwell time for both the electron beam and ion beam windows, as shown in in Fig. B.2 (b). Higher resolution and longer dwell time both lead to longer image capture times.

4. Adjust the milling current to achieve a reasonable milling time for each cross-section (about 15 minutes to mill a 100×100 µm alkaline battery cross section). Here, the ion beam is at 30 KV and 21 nA.

5. Draw a pattern (yellow rectangle in Fig. B.2 (c), right bottom window). Move the pattern to the desired milling area, but the yellow box has to be within the blue box, or else an error warning will appear. Here we obtained dimensions of 90 (width) × 80 (height), and took images every 0.5 µm. The depth is set at 40 µm, but the ion beam actually mills much deeper than 40 µm because we used the Silicon application, which means the ion beam treats the material as if it were silicon. Because silicon is harder than EMD and graphite, the beam ends up milling about 200 µm deep when set to 40 µm.
6. Mill a fiduciary mark which serves as a reference for when the ion beam re-locates after each slice. There are two options for fiduciary areas: either at the top right or top left. This is selected using the setting in the bottom left of Fig. B.2 (c).

7. Deposit platinum by checking “make protective layer” in Fig. B.2 (d). Right click and heat up the platinum if “make protective layer” is not available. The pattern box turns green when platinum deposition is available.

8. For obtaining a larger image area, drag “electron beam shift” to its upper limit and “ion beam shift” to its bottom limit. Beam shift is shown in the right panel illustrated in Fig. B.2 (c). Our 3D FIB/SEM data sets are collected in this manner.

9. Review all the settings in Fig. B.2 (e), and hit the “run” button if everything is correct. Otherwise, go back and adjust settings.

Finishing Steps

1. Stop the milling process.

2. Put the electron and ion beams to sleep.

3. Vent the chamber (stage will move back to its un-tilted state automatically), then move the stage to the sample exchange position.

4. Take the sample out and vacuum the chamber until the microscope icon in the bottom right of Fig. B.1 turns green.
Figure B.2: Illustration of Slice and view software. Explanations of each sub-figure are found in the body text of the appendix.
Appendix C
Program Scripts

This work involves a variety of programming in Matlab, C++ and FORTRAN. Not all program scripts developed in this work are attached in the appendix below, for the purpose of reducing the number of printed pages. Only sample scripts are presented for those codes which are significant part of this work. One can contact Professor Dean Wheeler for complete program scripts by emailing dean_wheeler@byu.edu.

C.1 Stretch and Alignment (Matlab)

The Matlab script for image stretching and alignment has two versions: one for a laptop, and another for a supercomputer. A supercomputer is preferred for large sizes of images. We processed our FIB/SEM image series with a supercomputer. One can use the laptop version of the scripts for a series of less than 100 images and if each image is around $2048 \times 2048$ pixels (at least 8 GB of RAM is necessary). Image stretching and alignment work was collaborated with the porous media group in IMTEK at the University of Freiburg.

The following is a section of the input script used to stretch, align and crop a FIB/SEM image series with a supercomputer.

```matlab
nameFinalFile = 'Duracel_Sample'; %% !!!!!!! change this name according to the sample
fibcameraAngle = 54;
%% code will open top view pictures, align, and crop them
folder_top_view='panfs/pan.fsl.byu.edu/scr/usr/81/danilob/Crop/TiffImages/topview';
% !!!!!!! Write address of top view images
folder_front_view='panfs/pan.fsl.byu.edu/scr/usr/81/danilob/Crop/TiffImages/frontview';
% !!!!!!!write address of front view
```
top_view_Address = strcat(folder_top_view,'/*.tif'); %browse the folder where the top images are.
front_view_Address=strcat(folder_front_view,'/*.tif');
I=IOReadImages2(top_view_Address); %reads the images and creates a stack
[Disp,ImStack]=ChunkAlignmentCrossCorrelationPicker(I,4,10,124,832,950); %!!!! add the cropping information in last 4 input values minRow ,maxRow, minCol, maxCol

% code will save the images on the folder path you select
[Height Width Number] = size(ImStack); %size information about picture
ImageRange = [1:Number].';
mkdir(folder_top_view,'topaligned');
savetopaligned = strcat(folder_top_view,'/topaligned');
savetop = strcat(savetopaligned,'/topaligned');
IOWriteImages(ImStack, ImageRange,savetop,'.tif'); %save top images aligned

%% code will take the original image and see size of top view pixels as well as the cutting distance between pictures
fprintf('n Calculating cutting distance on top view...n');

Following part will find the pixel size of top view images
loadalignedimages = strcat(savetopaligned,'/*.tif');
alignedpictures = dir(loadalignedimages);
oldpictures = dir(top_view_Address);
string1=strcat(folder_top_view,'/',oldpictures(2).name)
fileID = fopen(string1);
pictureFile = textscan(fileID,'%s');
x=pictureFile{1,1};
ind=strfind(x,'PixelWidth');
position=find(~cellfun(@isempty,ind));
stringwithPixelSize = x{position(1),1};
C = strsplit(stringwithPixelSize,'=');
PixelSizeTopView = str2double(C); %contains the pixel size of the top view
CuttingDistance = PixelSizeTopView*distance/40; %%we will use this value to do the stretching.

rmdir(strcat(folder_top_view,'/topaligned'),'s'); %this line will delete the top view folder
%% This part of the code will allow one to stretch and align the images.
fprintf('n Streaching and aligning front view...n');
I=IOReadImages2(front_view_Address); %reads the images and creates a stack
[Disp,ImStack]=ChunkAlignmentCrossCorrelationPicker(I,4,1784,2240,3104,3624); %!!!!!!! change cropping pixels, last 4 values in order minRow, maxRow, minCol, maxCol
C.2 Image Segmenting (Matlab)

The following is a section of the input script used to segment FIB/SEM images.

```matlab
function res = serena_analysis_top(input)
    % Get and show the original image
    figure(1);
    % input = rgb2gray(input); % If this outputs an error then the image you have is probably already in grayscale.
    input = double(input) / 255;
    A_orig = input; imshow(A_orig);
    % Obtain useful image information and balance the image
    [height width] = size(A_orig);
    xv = zeros(width,1);
    for x = 1:width
        xv(x,1) = (x/width) ^ 3;
    end
    for x = 1:width
        for y = 1:height
            A_orig(y,x) = A_orig(y,x) + (xv(x,1) * 0.1);
        end
    end
    % figure(2);
    % imshow(A_orig);
    [Xout, Yout, Zout] = prepareSurfaceData(1:height, 1:width, A_orig);
    f = fit([Xout, Yout], Zout, 'poly11');
    for h = 1:height
        grad_image(h,1:width) = feval(f, h, 1:width);
    end
    end
    % figure(2);
    % imshow(A_orig);
    balanced_image = double(A_orig) ./ grad_image;
    balanced_image = mat2gray(balanced_image);
    % figure(2); % imshow(balanced_image); % plot(balanced_image(10,:));
    % Use medfilt2 to make the image less grainy
    h_height = 5; h_width = 3; % figure(3);
    median_filtered = medfilt2(balanced_image, [h_height h_width], 'symmetric');
    pretty_image = mat2gray(median_filtered);
    % Adjust the contrast of the image. This is an attempt to normalize all the images.
    newRange = 1.0; %// choose the new maximum. (new minimum always at 0.0)
    imgMin = double(min(pretty_image(:)));
    imgMax = double(max(pretty_image(:)));
    pretty_image = (pretty_image - imgMin) / (imgMax - imgMin) * newRange;
    % Adjust the brightness of the image. This is an attempt to normalize all % the images.
    Our target average luminousity (mean) is 0.4.
    mean = 0;
    for y = 1:height
```

199
for x = 1:width
    mean = mean + pretty_image(y,x);
end
end
mean = mean / (height * width);
factor = 0.4 / mean; factor_pretty_image = pretty_image * factor;
% imshow(pretty_image); % The range filter! This is great because it helps make edges and image
% changes very clear. It also tends to emphasize the 'stripes' the FIB leaves on the active material which is useful.
range_image = rangefilt(pretty_image);
% imshow(range_image, []); % % Make nice image % figure(60);
sharp_balanced_image = imsharpen(balanced_image);
% imshow(sharp_balanced_image,[]);
   h = ones(15,1);
filtered_image = imfilter(sharp_balanced_image, h, 'replicate');
filtered_image = mat2gray(filtered_image);
new_image = sharp_balanced_image - filtered_image; new_image = mat2gray(new_image);
entropy_image = entropyfilt(new_image);
   entropy_image = entropy_image / max(max(entropy_image)); % imshow(entropy_image, []);
   h = ones(35,2);
filtered_image = imfilter(balanced_image, h, 'replicate');
filtered_image = mat2gray(filtered_image);
filtered_image = imadjust(filtered_image, [0 1], [0 1], 0.7); % imshow(filtered_image, []);
C.3 Compute Conductivity of 3D Structure (FORTRAN)

The following is a section of the input script used to compute conductivity for 3D structures.

c set up periodic boundary conditions
c on outside of cuboid
c direction +x
 nabor(1,site) = (k-1)*NX*NY+(j-1)*NX+mod(i,NX)+1
c direction -x
 nabor(2,site) = (k-1)*NX*NY+(j-1)*NX+mod(i-2+NX,NX)+1
c direction +y
 nabor(3,site) = (k-1)*NX*NY+mod(j,NY)*NX+i
c direction -y
 nabor(4,site) = (k-1)*NX*NY+mod(j-2+NY,NY)*NX+i
c direction +z
 nabor(5,site) = mod(k,NZ)*NX*NY+(j-1)*NX+i
c direction -z
 nabor(6,site) = mod(k-2+NZ,NZ)*NX*NY+(j-1)*NX+i

c *********************************************************
c perform iterations to solve for relative node potentials
c using finite difference equations
c
stopflag = .false.
iter = 0
do while (.not. stopflag)
 iter = iter + 1 unbal = 0

c update timestep parameter
 TS = TSf +(TS-TSf)*(1.-rate*float(ngrid)**(-0.5))

c loop over nodes
c
site1 = 1, ngrid

c c change order of solving equations to optimize for speed
 site = ngrid - abs(ngrid-2*site1+1) 1 + floor((2.*site1-1.5)/ngrid)

c c skip site potential update if zero conductivity/connectivity
 if (kttot(site) .lt. 99.*eps) cycle

c c potential of site that would exactly satisfy the node equation;
c it is a weighted average of neighbor potentials
 potlsat = 0.
do j1 = 1, 6 !loop over neighbors
 potlsat = potlsat + kpair(j1,site) 1 *(potl(nabor(j1,site))+field(j1))
 enddo


c c update site potential with use of timestep parameter
 potlold = potl(site)
potl(site) = TS*potlsat + (1.-TS)*potlold

c c count number of nodes with potential errors above threshold
if (abs(potsat - potlold) .ge. threshold)
1 unbal = unbal + 1
enddo ! end loop over nodes

c ********************************************************* c

c now calculates effective conductivity for three different

c sampling planes normal to the field direction

c (assumes NX,NY,NZ are each 3 or greater)

c where keff = L*I/(A*deltaV) c

keff1 = 0.D0
keff2 = 0.D0
keff3 = 0.D0
j1 = 2*dir-1 !neighbor across/opposite the plane

area = dfloat(ngrid)/dfloat(nnode(dir))
do site = 1, ngrid
if (ktot(site) .lt. 99.*eps) cycle !skip site if zero conductivity
post = position(dir,site)
if (post .eq. nint(nnode(dir)/6.)) then !first plane
kp(j1) = kpair(j1,site)*ktot(site)/shape(j1)
keff1 = keff1 + kp(j1)/area *(potl(nabor(j1,site)) - potl(site) + 1.0)
elseif (post .eq. nint(nnode(dir)/2.)) then !second plane
keff2 = keff2 + kpair(j1,site)*ktot(site)/shape(j1)/area *(potl(nabor(j1,site)) - potl(site) + 1.0)
elseif (post .eq. nint(nnode(dir)*5./6.)) then !third plane
keff3 = keff3 + kpair(j1,site)*ktot(site)/shape(j1)/area *(potl(nabor(j1,site)) - potl(site) + 1.0)
endif
enddo ! end loop over nodes

c calculate mean and std dev of mean for 3 sampling planes c
keff = (keff1 + keff2 + keff3)/3.D0
kerr = sqrt(abs((keff1**2+keff2**2+keff3**2)/3.D0-keff**2)/3.)

write(6,fmt='(2(A,F10.4))') ' k = ',keff,' +-',kerr

c c warn if keff not fully converged/consistent c
if (kerr .gt. (0.01*keff + 10.*threshold))
then write(6,*') conductivity not well-converged:'
write(6,fmt='(3(A,F10.4))')' k1=',keff1, 1 ' k2=',keff2, 1 ' k3=',keff3
endif
return
end
C.4 Stochastic Grid Model (FORTRAN)

The following is part of the stochastic grid model scripts. The following script is the algorithm that increases connections of carbon additive domain groups.

```fortran
    do i5 = 1, vol*100 ! find first carbon site
        CALL RANDNUM(IRR,Rnum)
        site1 = MOD(IRR,vol)+1
        id1 = domain(site1)
        if (id1 .eq. 1) exit
    enddo
    mass1 = 1 !mass accumulator
    mx1 = 0 !x position mass accumulator
    my1 = 0 !y position mass accumulator
    mz1 = 0 !z position mass accumulator
    do i5 = 1, vol*100 ! find sphere containing more than 70% carbon
        do i = -radius, radius
            do j = -radius, radius
                do k = -radius, radius
                    if (i*i+j*j+k*k .gt. radius*radius) cycle !reject nodes not inside sphere
                    site1r = mod(i-1+length+position(1,site1),length)*area +
                            mod(j-1+length+position(2,site1),length)*length +
                            mod(k-1+length+position(3,site1),length) + 1
                    if (domain(site1r).eq. 1) then !neighbor is carbon too
                        mass1 = mass1 + 1 ! mass1 is the volume
                        mx1 = mx1 + mod(i-1+length+position(1,site1),length)
                        my1 = my1 + mod(j-1+length+position(2,site1),length)
                        mz1 = mz1 + mod(k-1+length+position(3,site1),length)
                    endif
                enddo
            enddo
        enddo
    if (mass1 .gt. 0.7*4.18*radius**3) then ! change this
        exit
    else i1 = mx1/mass1
        j1 = my1/mass1
        k1 = mz1/mass1
        site1 = mod(i1-1+length,length)*area 1 + mod(j1-1+length,length)*length 2 + mod(k1-1+length,length) + 1
    endif
    enddo
    enddo
    enddo
    if (mass1 .gt. 0.7*4.18*radius**3) then ! change this
        exit
    else i1 = mx1/mass1
        j1 = my1/mass1
        k1 = mz1/mass1
        site1 = mod(i1-1+length,length)*area 1 + mod(j1-1+length,length)*length 2 + mod(k1-1+length,length) + 1
    endif
    enddo
    do i5 = 1, vol*100 ! start loop to find second carbon site
        CALL RANDNUM(IRR,Rnum)
        site2 = MOD(IRR,vol)+1
        id2 = domain(site2)
```
if (id2 .ne. 1) cycle !reject immediately if not carbon

c c find nearest image distance between two sites
dx = position(1,site1) - position(1,site2)
dy = position(2,site1) - position(2,site2)
dz = position(3,site1) - position(3,site2)
dx = dx - length*int(dx*2/length) ! applied modeling boundary theory
dy = dy - length*int(dy*2/length)
dz = dz - length*int(dz*2/length)
dist2 = dx*dx + dy*dy + dz*dz

c accept second carbon site if far enough from first site
if (dist2 .gt. 9*radius*radius) exit
enddo

c c try to find cluster centers and amount of other carbon
inside the spheres centered on each carbon site
c mx1 documents the relative position to site 1
mass1 = 1 !mass accumulator
mx1 = 0 !x position mass accumulator
my1 = 0 !y position mass accumulator
mz1 = 0 !z position mass accumulator
mass2 = 1 !mass accumulator
mx2 = 0 !x position mass accumulator
my2 = 0 !y position mass accumulator
mz2 = 0 !z position mass accumulator

do i = -radius, radius
do j = -radius, radius
do k = -radius, radius
if (i*i+j*j+k*k .gt. radius*radius) cycle !reject nodes not inside sphere
site1r = mod(i-1+length+position(1,site1),length)*area +
        mod(j-1+length+position(2,site1),length)*length + mod(k-1+length+position(3,site1),length) + 1
if (domain(site1r).eq. 1) then !neighbor is carbon too
mass1 = mass1 + 1 ! mass1 is the volume
mx1 = mx1 + i
my1 = my1 + j
mz1 = mz1 + k
endif
site2r = mod(i-1+length+position(1,site2),length)*area +
        mod(j-1+length+position(2,site2),length)*length + mod(k-1+length+position(3,site2),length) + 1
if (domain(site2r).eq. 1) then !neighbor is carbon too
mass2 = mass2 + 1
mx2 = mx2 + i
my2 = my2 + j
mz2 = mz2 + k
endif
enddo
ENDDO
ENDDO

C now processes data to find effective radii of
C carbon clusters found within each sphere

RADIUS1 = NINT(((0.239*MASS1)**0.3333) / (4*PI*RADIUS**3)) = MASS1
RADIUS2 = NINT(((0.239*MASS2)**0.3333) / (4*PI*RADIUS**3))
DIST = RADIUS1 + RADIUS2

C make subspheres of same radius where one is centered on
C the smaller carbon cluster and other one is moved adjacent
C to the larger carbon cluster

IF (MASS1 .LE. MASS2) THEN ! then sphere 1 has smaller cluster
RADIUS = RADIUS1
I1 = MX1/MASS1
J1 = MY1/MASS1
K1 = MZ1/MASS1
RR2 = SQRT(MX2**2 + MY2**2 + MZ2**2 + EPS)
I2 = NINT(MX2*(1./MASS2-DIST/RR2)) ! MX2/RR2 create unit direction
J2 = NINT(MY2*(1./MASS2-DIST/RR2))
K2 = NINT(MZ2*(1./MASS2-DIST/RR2))
ELSE ! sphere 2 has smaller cluster
RADIUS = RADIUS2
I2 = MX2/MASS2
J2 = MY2/MASS2
K2 = MZ2/MASS2
RR1 = SQRT(MX1**2 + MY1**2 + MZ1**2 + EPS)
I1 = NINT(MX1*(1./MASS1-DIST/RR1))
J1 = NINT(MY1*(1./MASS1-DIST/RR1))
K1 = NINT(MZ1*(1./MASS1-DIST/RR1))
ENDIF

C now recenter both sites: one in the middle of the
C smaller carbon cluster, the other adjacent to the
C larger carbon cluster

SITE1 = MOD(I1-1+LENGTH+POSITION(1,SITE1),LENGTH)*AREA +
MOD(J1-1+LENGTH+POSITION(2,SITE1),LENGTH)*LENGTH +
MOD(K1-1+LENGTH+POSITION(3,SITE1),LENGTH) + 1

SITE2 = MOD(I2-1+LENGTH+POSITION(1,SITE2),LENGTH)*AREA +
MOD(J2-1+LENGTH+POSITION(2,SITE2),LENGTH)*LENGTH +
MOD(K2-1+LENGTH+POSITION(3,SITE2),LENGTH) + 1

C C now that we have two satisfactory sphere centers, we
C identify all nodes within radius of each site (a sphere),
C and swap identities of the nodes in each sphere having
C the same relative position.

DO I = -RADIUS, RADIUS
DO J = -RADIUS, RADIUS
DO K = -RADIUS, RADIUS
if (i*i+j*j+k*k .gt. radius*radius) cycle !reject nodes not inside sphere
site1r = mod(i-1+length+position(1,site1),length)*area +
mod(j-1+length+position(2,site1),length)*length +
mod(k-1+length+position(3,site1),length) + 1
site2r = mod(i-1+length+position(1,site2),length)*area +
mod(j-1+length+position(2,site2),length)*length 1 +
mod(k-1+length+position(3,site2),length) + 1
id1r = domain(site1r)
domain(site1r) = domain(site2r)
domain(site2r) = id1r
endo
dendo
endo
endif !done with secondary move