Microstructural evolution of tin alloy anodes for lithium ion batteries

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MICROSTRUCTURAL EVOLUTION OF TIN ALLOY ANODES FOR LITHIUM ION BATTERIES

by

JACOB N. ADAMS

A THESIS

Submitted in partial fulfillment of the requirements for degree of Master of Science in Engineering in The Department of Mechanical and Aerospace Engineering to The School of Graduate Studies of The University of Alabama in Huntsville

HUNTSVILLE, ALABAMA

2020
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We, the undersigned members of the Graduate Faculty of The University of Alabama in Huntsville, certify that we have advised and/or supervised the candidate on the work described in this thesis. We further certify that we have reviewed the thesis manuscript and approve it in partial fulfillment of the requirements for the degree of Master of Science in Engineering.
ABSTRACT
The School of Graduate Studies
The University of Alabama in Huntsville

Degree: Master of Science in Engineering

College/Dept.: Mechanical and Aerospace Engineering

Name of Candidate Jacob Nathaniel Adams

Title: Microstructural Evolution of Tin Alloy Anodes for Lithium Ion Batteries

There is capability for advancement of the electrochemical capacity of lithium ion battery (LIB) electrodes by utilizing the high capacity of tin (Sn) in Sn alloy electrodes. However, the destructive effects of volumetric expansion must be mitigated in order to sustain this high capacity during extended cycling. One of the ways these effects can be mitigated is by alloying Sn with more malleable metals. Through this approach the electrode can attempt to accommodate the severe volumetric expansion and related strain.

In order to evaluate the effectiveness of alloy electrodes, ex situ X-ray microtomography data of cycled Cu$_6$Sn$_5$ pellets was used to quantify the microstructural changes that occur during lithiation and delithiation. The microtomography data was segmented into three distinct phases to evaluate phase size distribution (PSD), surface area to volume ratio, tortuosity, connectivity, and interface area between phases. When evaluating the PSD of each electrode sample, it can be seen that the electrodes lithiated and then delithiated showed the most substantial reduction in overall phase sizes compared to the other samples. This suggests that full lithiation of the Sn present in the alloy electrodes followed by partial delithiation of the Li$_{4.4}$Sn to Li$_2$CuSn can cause substantial microstructural changes related to volume expansion on lithiation and structural collapse upon delithiation. When considering other microstructural characteristics, the tortuosity for the electrodes and then
delithiated show the highest tortuosity factor compared to other samples. These results show that in addition to the mechanical degradation of the electrodes, excessive volume expansion can also influence transport networks in the active material and supporting phases of the electrode. While based on studies the active-inactive alloy Cu₆Sn₅ for lithium ion battery applications, the insights obtained are expected to be applicable to other alloy electrodes and battery chemistries.
The work presented herein would not have been possible without the support and guidance from Dr. George Nelson. He has patiently worked with me for many hours and I greatly appreciate it. I would also like to thank Dr. Yu Lei and Dr. Guangsheng Zhang for reviewing this work.

To all of my family, especially my wife:

Thank you for all of the support you have given me through the years to help me achieve this goal.
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CHAPTER 1:

Introduction

Li-ion batteries (LIBs) play a key role in current day and future technology. Our existing and future technology hinges on the ability to store and transport energy more efficiently. Li-ion batteries have a relatively high energy density and a decreasing cost which has made LIBs the choice for many applications today and sparked an interest in the research of LIBs. Graphite anodes are the most common choice for many commercial Li-ion batteries. However, when the capacity of graphite (372 mAhg$^{-1}$) is considered it becomes clear that there is room for improvement. For LIBs, high-capacity anode development based on tin (Sn) and silicon (Si) can achieve an order of magnitude higher specific capacity compared to the conventional graphite anode. The Li storage capacity of Sn has a theoretical value of 991 mAhg$^{-1}$ and the Li storage capacity of Si has a theoretical value of 3579 mAh/g which are both significantly higher than that of graphite [1–6]. Both of these high capacity options have failure mechanisms that must be mitigated in order to utilize their high capacity. Sn will be the primary interest herein. Pure Sn undergoes excessive (300%) volume change when alloying with lithium. This volume change causes dramatic structural changes and leads to capacity fade during electrode cycling. To overcome the adverse effects of lithiation and volume expansion, various routes, such as developing alloys and nano-materials, have been explored to accommodate expansion and reduce crack formation [1,7–18]. Among these routes, Sn-
based intermetallic compounds, Sn$_x$M$_y$ (M: Cu, Ni, Fe, Co), have been explored where the lithium alloying reaction forms a Li-Sn alloy within a relatively ductile host matrix that accommodates strain [2]. For example, Cu-based porous foam structures with Sn can serve the dual purpose of electrode and current collector [2,19–23]. The porous foam architecture is believed to allow shorter lithium transport pathways and increase electrochemically active interfacial area, resulting in improved electrochemical performance [2]. However, substantial capacity fade has been observed in intermetallic alloy anodes during cycling.

Capacity fade in intermetallic electrodes has been attributed to several potential mechanisms, which include: (1) expulsion of inactive material from the composite microstructure; (2) mechanical disintegration of microstructure; (3) Li$_2$O formed from metal oxide impurities; and (4) solid electrolyte interface formation and reformation after mechanical disintegration. The first of these mechanisms relates to the chemical reactions that occur during lithiation [24]. Above 0.2 V vs. Li/Li$^+$, an intermediate ternary alloy, Li$_2$CuSn, is formed during lithiation of Cu$_6$Sn$_5$, and some expulsion of Cu from the alloy matrix occurs. Cycling down to 0 V vs. Li/Li$^+$ leads to complete Cu expulsion from the alloy material. Mechanical disintegration also occurs during lithiation. For the first reaction step a volume change of ~45% has been noted, while full lithiation increases expansion to ~180% [2]. This expansion fractures the active material and may lead to microstructural collapse after extended cycling [25]. Such behavior has been observed for particle-based and foil electrodes [20,26] as well as electrodes employing more novel mesoporous structures [2,21–25]. The content herein focuses on the observation and characterization of the microstructural changes that are introduced to Cu$_6$Sn$_5$ electrodes.
during various cycling conditions. Tomography, both on the micro and nano scale, is an effective way of evaluating and, in many cases, quantifying material structures. Being able to capture an image of the structure of materials at various states under various conditions allows us to attribute the reason for particular structural changes in materials. The tomographic method used herein is X-ray microtomography (µCT). µCT is used to image the 3D microstructure of samples extracted from pristine and cycled electrodes. The reconstructed samples are segmented using grayscale thresholding informed by the histograms of background and pristine sample regions. The continuous phase size distributions (PSD), specific surface areas, interface areas, connectivity, and tortuosity of lithiated, non-lithiated, and pore phases are compared.

In chapter 2, the basic importance of LIBs and increasing our energy storage capabilities is described. Some of the various material options for potentially increasing the capacity of our modern LIBs and some background about these material options such as manufacturing processes that have been used to attempt to mitigate the adverse effects seen by cycling are discussed as well. Lastly, chapter 2 discusses, in more detail, some of the previously developed methods for imaging and characterizing the microstructures herein. In chapter 3, the methodology for the analysis herein is described. This chapter includes a description of the cycling conditions that are being tested, sample images, sample region sizes, segmentation techniques, and also a description of the various calculations that were done on the microstructure in order to characterize the structural changes. Chapter 3 also includes additional information on how the characterization code was implemented for the samples herein. Chapter 4 includes all of the analysis results from the characterization calculations herein. These results include Phase Size
Distribution, Continuous Phase Size Distribution, Specific Surface Area, Interfacial Area, Tortuosity, and Connectivity. These results are utilized to attribute the microstructural changes of the tested anodes to cycling characteristics. Finally, chapter 5 concludes the paper and summarizes the results herein.
CHAPTER 2:

Literature Review

2.1 Lithium Ion Battery Structure and Function

Lithium ion batteries are composed of a positive electrode (cathode) and a negative electrode (anode) that are separated by an electrolyte which allows ionic transport and prevents electron transport. In these electrodes redox reactions take place once the two electrodes are externally connected to allow current flow between them. Typically, LIBs consist of multiple cells that each contribute to the total electrochemical storage of the battery. It is this current flow that is tapped into to be used for power [40]. An example schematic of a single LIB cell is shown in figure 2.1.

![Figure 2.1: Basic schematic of a discharging lithium ion battery [1]]
Lithium (Li) intercalation compounds such as Lithium Cobalt Oxide (LiCoO₂), often called LCO, are typically used for cathode materials. These cathode materials are often characterized by a layered structure, such as LCO, NMC, LNMO, and NCA. However, lithium transition metal oxides with spinel and olivine crystal structures may also be applied. Graphitic carbons are typically the choice material for negative electrodes in commercial LIBs. Both these types of positive and negative electrode materials are able to reversibly insert and remove Li ions within the crystal lattice of the active material, which allows the needed change in electrochemical potential required for the electrochemical energy conversion [41]. These insertion and removal processes are referred to as intercalation and deintercalation, respectively. When the LIB is being charged, lithium deintercalates from the cathode and enters the electrolyte surrounding the cathode active material. The Li⁺ ions are then transported through the electrolyte (typically nonaqueous) from the cathode to the anode. After the Li⁺ ions are transported to the anode, they are intercalated into the structure of the graphite active material. This is a continual process that occurs throughout the course of a battery charging. Upon discharge, the charging process is reversed, and Li is deintercalated from the anode structure, transported through the electrolyte back to the cathode, and intercalated into the cathode once more. [41].

### 2.2 Volumetric Effects on Anodes

As stated earlier, LIBs rely on the transport and storage of Li ions. One area of potential advancement is in the transport and storage of Li ions in the anode material.
Historically, the most commercially successful electrode material chemistry has been intercalation-type electrodes. As stated earlier, this typically consists of transition metal oxide cathodes, such as LCO, and graphite anodes. These common electrode materials have proven to be capable of providing sufficient Li ion transport while still supporting multiple charge and discharge cycles contributing to the robustness and longevity of the battery [42].

Graphite has proven to be a superior choice when regarding the structural integrity of the anode due to its low volumetric expansion. This low volumetric expansion is an important factor in the longevity of the battery system by yielding a lower and less degrading strain in the anode upon cycling [42]. The lower volumetric expansion and strain in the anode material is important from multiple perspectives. First, high strain in the anode structure can yield in a high enough stress that results in microstructural defects to the material such as facture and pulverization of the anode material leading to a negative effect in material properties such as a decrease in the bulk diffusivity of the material [42]. Second, high volumetric expansion can lead to a high strain in the solid electrolyte interphase (SEI) layer. The SEI is a critical electrode phase formed upon the interface between the anode material and the electrolyte. This layer protects the further decomposition of the electrolyte and functions like the electrolyte by being an ionic conductor and an electronic insulator. Lithium can move through the SEI, while the layer prevents degradation of the electrolyte. A high strain in the SEI layer due to volumetric expansion and pulverization can form electrolyte solvent-permeable defects. These electrolyte solvent-permeable defects can lead to the continuous growth of SEI upon the electrolyte reduction at a low anode potential. This can lead to the
irreversible consumption of Li from the cell and reduce the capacity of the cell with cycling [43].

The current graphite anodes are sufficient for reliable ionic transport and storage and have a very low volumetric change upon intercalation and deintercalation of Li. However, when compared to other potential anode materials they provide a relatively low specific capacity of approximately 372 mAh/g [44]. This low specific capacity of graphite is one limiting factor in the overall capacity of the battery system.

2.3 High Capacity Anode Materials

In hopes of improving upon the anode capacity, materials such as Si, Sn, and Ge have been highly researched due to their relatively high theoretical specific capacities. The respective theoretical specific capacities of Ge, Si, and Sn are 800 mAh/g, 3579 mAh/g, and 990 mAh/g [48]. These significantly higher specific capacities make it clear why these materials are considered for the usage as anode materials. Although these materials are very appealing due to their high capacities, there are still unique tradeoffs that are made with each of these promising materials that must be mitigated.

2.3.1 Germanium

Germanium (Ge) is a relatively expensive material, but it has still sparked interest in Li ion research due to high conductivity and Li diffusivity. Early research of small Ge particles being utilized in anodes shows that the lithiation process for Ge is relatively isotropic and thus the internal stresses due to volumetric expansion are reduced. This helps prevent material degradation upon cycling such as cracking. This isotropic behavior
introduces one advantage that Ge can have over other high capacity anode materials. Ge can support the usage of larger particle sizes that are typically avoided to mitigate material degradation that can occur upon lithiation and delithiation due to anisotropic volumetric expansion of some other high capacity anode materials such as Si [42].

2.3.2 Silicon

Silicon (Si) is one of the most widely studied anode materials due to the extremely high theoretical specific capacity of 3579 mAh/g [42]. Apart from the high theoretical specific capacity, Si has a relatively low discharge voltage, is the second-most abundant element that can be found in the earth’s crust, and is considered environmentally benign [38]. Although Si has many ideal characteristics, there are still multiple failure mechanisms that must be mitigated for the application of Si as an anode material [42]. The primary failure mechanisms of Si electrodes are material pulverization, continuous SEI growth, and morphology and volume change of the entire Si electrode [38]. These mechanisms are mostly linked to the excessive volumetric expansion of Si on lithiation. A contributing factor to the material degradation due to large volumetric expansion is that if the Si is crystalline, this large expansion will occur anisotropically. This results in an internal stress build up in the material and often leads to plastic deformation at approximately 40% overall capacity [42]. Nano-structures are utilized to help mitigate the negative effects that occur due to the anisotropic volumetric expansion by ways such as relieving stress at the surfaces as well as providing more void space to allow for the excessive volumetric expansion [42]. Some of the most successful nano-structures include Si nanowires, Si nanoparticles, and hollow Si nanostructures. Si
nanowires primarily mitigate the volumetric expansions of Si through the significant void space that separates the adjacent nanowires. Si nanoparticles accommodated the large volumetric expansions by driving the particle size small enough to allow for the large volumetric strains without mechanical fracture. The hollow Si nanostructures accommodate the volumetric expansion primarily through the empty interior space [38]. Although these nano-structures have been shown to be effective in mitigating some of the adverse effects seen during lithiation, there are still draw backs from a practicality standpoint. The cost required to produce these nano-structured materials are currently very high and there can often be difficulty in scaling up the production of these materials to a larger, but necessary, scale.

2.3.3 Tin

Like silicon, tin (Sn) is appealing for its specific capacity, but it also undergoes large volumetric expansion upon lithiation. Sn has a significantly lower specific capacity than that of Si, but the volumetric capacities are comparable with Sn and Si having volumetric capacities of 7246 mAh/cm$^3$ and 9786 mAh/cm$^3$, respectively [44]. The theoretical capacity of Sn has yet to be reached with stable cycling due to the material degradation that occurs upon lithiation and delithiation. The lithiation process causes Sn to expand between about 100% to 300% over the course of lithiation. This large volumetric expansion is not totally unique to Sn, but unlike Ge and Si, Sn has a very low melting point. So, when Sn is at room temperature, it is at approximately 60% of its melting point. This causes the Sn atoms to be much more mobile and crystallize much easier than Ge or Si. This ease of crystallization is an additional factor in the fracturing of
lithiated Sn during the excessive volumetric expansion [42]. The destructive effects of volumetric expansion must be mitigated in order to sustain this high capacity during extended cycling. One of the ways these effects can be mitigated is by alloying Sn with more malleable metals [2]. By forming active-inactive alloys, the electrode can attempt to accommodate the severe volumetric expansion with a malleable inactive metal such as copper, while retaining some of the high capacity of Sn [2]. Since expansion is mitigated with an inactive metal, there are losses in the potential capacity of the anode. Another way to accommodate the extreme volumetric expansion of Sn is by forming an alloy with another active metal. This active-active approach results in a higher theoretical capacity than the active-inactive alloy, since the secondary metal participates in the lithiation process [49].

2.3.3.1 Active-Inactive Alloys

In hopes of mitigating the negative effects of volumetric expansion, while still harnessing the larger capacity of Sn, Sony pursued the utilization of an active-inactive tin-cobalt (Co) alloy that results in an increased life cycle and capacity over a pure Sn anode [40]. In this configuration, the Sn-Co anode is lithiated to form Li-Sn-Co, Li-Sn, and potentially amorphous Co phases. Then, upon delithiation of the anode, the Sn will re-alloy with Co rather than reforming a pure Sn phase. This process is believed to have caused the longer life cycle of Sn-Co anodes over pure Sn anodes by not forcing the Sn particles to reform into the pure Sn phase upon delithiation [45].

Another way that the fracturing nature of lithiated Sn is being mitigated is through the alloying of a ductile inactive matrix to the brittle Sn. This design is used to buffer the
volumetric expansion and fracture that occurs with pure Sn while still utilizing the higher
capacity of Sn. There are multiple intermetallic compounds that have been suggested as
promising electrode materials. One of these promising compounds is Cu₆Sn₅ [45].

Cu₆Sn₅ is an active-inactive intermetallic compound, the copper being the inactive
metallic component and the tin being the active metallic component. Although this is a
suggested promising electrode compound due to the theoretical properties and robustness,
this compound continues to show capacity fade upon cycling. Capacity fade in these
active-inactive electrodes has been attributed to several potential mechanisms, which
include: (1) expulsion of inactive material from the composite microstructure; (2)
mechanical disintegration of microstructure; (3) Li₂O formed from metal oxide
impurities; and (4) solid electrolyte interface formation and reformation after mechanical
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microstructural collapse after extended cycling [25]. Such behavior has been observed for
particle-based and foil electrodes [20,26] as well as electrodes employing more novel
mesoporous structures [2,21–25]. The content herein focuses on the observation and
characterization of the microstructural changes that are introduced to Cu₆Sn₅ electrodes
during various cycling conditions.
Other active-inactive alloys that have been pursued as viable options for anode materials are Sn-Ni/MWCNT and Si$_x$. In the case of the Sn-Ni/MWCNT, tin is combined with a combination of nickel and multiwalled carbon nanotubes (MWCNTs). In this material the nickel forms the inactive buffer providing excellent load bearing and MWCNT is used for its excellent conductivity capacity [49]. For the Si$_x$ the addition of nitrogen is to increase the cycling stability, but significantly lowers the irreversible capacity due to the essentially inactive nature of nitrogen [50].

### 2.3.3.2 Active-Active Alloys

Another way of mitigating the volumetric expansion of Sn by alloying is by using an active material to form an active matrix with Sn rather than in inert material. This allows for a higher specific capacity since both materials in the alloy have the ability to store Lithium ions. One example of an active-active alloy is SnSb. Different potentials instigate the lithiation/delithiation reactions of Sn and Sb and thus when one component is being lithiated, the other can act as a buffer to accommodate the volumetric expansion better than just Sn or Sb on their own. This results in a better electrochemical performance for the SnSb alloy than pure Sn or Sb. Although the electrochemical performance is better than the pure substances, SnSb alloys still show significant pulverization due to the volumetric expansion and contraction upon lithiation/delithiation. Recent research has suggested that controlling the particle size in the nanometer range is effective in solving these mechanical strain issues due to lithiation/delithiation [37]. Other active-active alloy materials that have been suggested are Al-Sn and silicon/carbon composite anodes. Both of these material suggestions are of two active metallic materials,
which enhances the theoretical capacity while attempting to accommodate structural changes upon cycling [51-52].

2.4 Image-based Materials Characterization

As noted in the previous text, there are many promising material combinations that can potentially be used for anodes in LIBs. However, in order to observe, understand, and mitigate failure mechanisms to advance material selection, it is necessary to observe and quantify structural changes that occur in materials as they undergo processes such as lithiation and delithiation. Characterization and analysis methods, based on imaging, are frequently used to determine properties and are necessary to understand the microstructure of materials and determine the functional impact that microstructural changes have. Previous work has been done with SEM imaging to characterize the growth behavior of tree-like interconnected silicon nanowires (SiNW). In this heritage work, growth attributed to Chemical Vapor Deposition (CVD) was analyzed from the SEM images and thus characterizing the growth of the SiNW [36]. Some methods of property determination that are of particular interest when observing the microstructural changes that occur during the lithiation and delithiation of materials include the measurements of individual phase volume fractions to quantify the volumetric amount of given phases relative to the entire volume, phase size distribution (PSD) that can describe the state of pulverization of a material, tortuosity which impacts the effective conductivity, and interfacial properties that influence the electrochemical reactions in a battery [46]. These measurements can be performed analytically on reconstructed three-dimensional (3D) micro-computed tomography (μCT) samples that are developed from
various material samples subjected to various lithiation and delithiation cycles. The characterization measurements that are determined for the different material samples can then be analyzed to compare the changes that occur in the microstructural characteristics for materials that are subjected to these lithiation and delithiation processes.

2.4.1 Micro-Computed Tomography (\(\mu\)CT) and Morphology

Microtomography is a key part in the analysis of material microstructure. Microtomography allows for the non-destructive look at the 3D structure of materials that can then be used to quantify a number of useful characterization parameters [42]. The 3D images that are used in the material characterization can be obtained in multiple ways. One common method for the construction of the 3D image is to use high resolution X-ray imaging to execute a \(\mu\)CT scan of a given sample. This \(\mu\)CT scan consists of completing a tomographic scan of a material sample and then rotating the sample some specified increment of rotation to then perform another scan at the new angle. This process can be iterated with equally space increments over a 180° or 360° span, depending on the nature of the incident X-ray beam, resulting in a set of many high resolution 2-dimensional (2D) images from all necessary angles of a sample. Once this \(\mu\)CT scan is complete, the set of 2D transmission images can be reconstructed into a 3D image. This 3D image can now be segmented based on gray values related to X-ray attenuation, and in some cases structural characteristics such as distance transforms, to produce images of individual material phases. These varied gray values result from the X-ray imaging process. During the imaging process, X-rays interact with the electron cloud of the material and each element and compounds thereof absorb X-rays to varied degrees. This produces varied contrast in
samples containing mixed materials and phases. Furthermore, at specific energies known as absorption edges the X-ray attenuation of a material changes. Generally, heavier elements, such as Cu and Sn, and their compounds absorb a greater amount of X-ray energy than light elements, such as Li, and their compounds. This creates a varied gray scale in the reconstructed image. It is this unique attenuation that occurs in each material that allows the different materials to be distinguished in a μCT samples [47]. The material identity can become further distinguished by then quantifying the darkness and lightness of the resulting pixels of an image, which is essentially using each material’s unique attenuation to be an identifier. This identification method enables the use the gray scale values of an image to distinguish between materials in a reconstructed μCT image. Once particular gray scale ranges are established for the particular materials, these 3D reconstructed μCT images can be segmented into the desired phases of material and pores yielding a binary representation of the material’s microstructure in the form of voxels. Following segmentation, the material phases are represented by a 3D matrix consisting of material identifying values. It is this segmentation that in turn enables the analysis of each homogenous phase of material inside of a heterogenous material sample.

2.4.2 Individual Phase Volume Fraction

The volume fraction of a phase or pore is simply the ratio of the volume occupied by that phase or pore to the volume of the entire sample. Volume fractions can be used to observe the relative volumetric amount that each phase contributes to the overall volume of a sample and can be important to issues such as percolation limits in multi-phase heterogeneous structures or measuring the extent of a reaction such as evaluating the
amount of lithiated products in an anode sample in order to determine the extent of lithiation that has occurred.

Characterization methods used to determine the individual phase volume fraction use reconstructed μCT data that is segmented to be a 3D representation of a multi-phase heterogeneous mixture. This 3D morphology consists of cubic voxels of a finite size and individual phase or pore distinction. Voxel counting routines are used to count the number of voxels of a given phase or pore and then compare that to the total number of voxels in the sample. Through the ratio of the number of voxels in a given phase to the total number of voxels in a sample, the volume fraction can be determined for that individual phase [46].

2.4.3 Phase Size Distribution (PSD)

The phase size distribution (PSD) can be used to examine the volumetric distribution of sizes, typically expressed as a radius, for a specific phase in a given sample. As stated earlier, the volume fraction for a given phase can be of use when trying to examine and describe particular transport phenomena. However, the volume fraction alone is limited in the examination of these transport phenomena. The PSD can be used to take a closer look at some of the details of a multiphase mixture. PSD is often used to describe a phase of a specified diameter’s contribution within a detailed phase-specific structure to the overall volume fraction of that specified phase. The PSD parameter can often be used to study the pulverized state of a given microstructure, the extent of fracture, or the size of pores supporting the transport of key reactants. For high capacity battery materials, this data is most useful when analyzing anode materials during
lithiation and delithiation to see if the PSD is decreasing, which denotes a pulverization is occurring upon the lithiation and delithiation of the material [48]. In a recent study on Sn-Co-C composite anodes, the PSD was calculated for the composite anodes with varying compositions. In this case the PSD was evaluated for each composite anode with different contents of metal cobalt. This indicated that the mesopores and macropores decreased as the cobalt content increased [39].

The PSD quantity can be calculated using multiple methods. One method, which is one of the methods used to achieve the PSD results found herein, utilizes ray shooting. Specifically, a discretization scheme built upon the Lattice Boltzmann method (LBM) is used to calculate ray lengths that can then be used to calculate a normalized continuous PSD value that represents the volume fraction of the phase paths contained for a given diameter and differential diameter. The LBM is a very mesh independent method that can, in itself, also be correlated with various transport phenomena as well. The LBM lends itself well to simulations on 3D segmented microtomography structures. In this method, each voxel in the structure has a set of 19 directional vectors that are interconnecting with surrounding voxels. These vectors are originated at the center of each voxel. This 19 directional vector set is used to discretize the geometric domain of a given phase of interest. This 19 directional vector set is used in the discretization to simplify the analysis by establishing a finite number of directions that are considered in the phase size calculations. [48]

In calculating ray lengths using an LBM discretization approach for the PSD characterization, voxels that lie upon the phase interfaces are of specific interest. At each voxel at the phase interface, a single ray is launched that is normal to that phase interface
using one of the 19 directions that are assigned to each voxel according to the LBM discretization. The ray that is initialized upon a phase interface is propagated along the specified direction until another phase is reached in the structure. The total ray length is then computed in terms of the number of voxels that are traversed by the ray and the voxel size is used to back out the physical length of the ray. This ray length is proportional to the cross-sectional area of a phase path and is used to portray the phase path diameters that, along with a specified differential diameter, define a histogram denoting the number of rays for a given diameter size and of a specific differential diameter. This histogram is then used to define the normalized PSD parameter that is of particular use in material characterization [48].

A second method, that can be used, calculates the continuous PSD (CPSD) by using the distance transform of a binary image and developing a particle mask. A modified watershed algorithm is used to fragment the particle mask. This modified watershed algorithm iteratively erodes the particle mask until certain defined fragmentation constraints are met for each particle. This makes use of a more adaptive fragmentation method rather than fragmenting particles at each concavity as with the traditional watershed method. This fragmentation process utilizes the Euclidean distance transform of the final fragmented particle mask to determine a 3D distance map. This 3D distance map catalogs the shortest distance to the surface at each location inside of the particle mask. This distance map yields the diameter of each particle, which is used to formulate the CPSD for the entire 3D image. This method for calculating the CPSD has been shown to correlate closely to the MIP method for phase/pore radii up to 50nm. This deviation at around 50nm is due to the MIP intrusion being affected by a phenomenon
known as the ink bottle effect. [33] This effect describes how pressure driven fluid intrusion porosimetry methods tend to favor characterization of narrow connections between larger pore regions. If an ink bottle were measured using MIP, the porosimetry method would skew toward measuring the mouth and neck of the bottle and undercount the contributions of the larger regions inside the bottle. Imaged based characterization of phase size eliminates this bias.

2.4.4 Connectivity

The connectivity or contiguity of a structure can be used to examine how well a structure is connected to itself. This examination can be useful, when combined with PSD and other properties, in evaluating the potential conductivity throughout a solid by the amount of structure that is interconnected. For high capacity anode materials, volume expansion and pulverization present a risk of isolating active material. This isolation can also be quantified with the connectivity.

The connectivity of a structure is evaluated by taking a reconstructed μCT data set, that has been segmented into a 3D representation of a multiphase structure, and utilizing a numerical painting scheme to label and count the connected voxels within a given phase. This technique produces results to determine the percentage of structure that is interconnected and thus producing a numerical measure of the connectivity or contiguity. This technique is then implemented for all principal directions of the sample (x, y, and z directions of a Cartesian coordinate system). Routines for calculating connectivity from X-ray tomography data have been developed by Grew et al. [46]
2.4.5 Tortuosity

The tortuosity of a given phase is a property that can be approximated through numerical methods performed on reconstructed µCT data that is segmented to be a 3D representation of a multi-phase heterogeneous mixture. The tortuosity along with the pore volume fraction can be used to calculate the empirical diffusivity factor of the porous phase of a material. This empirical diffusivity can then be used to describe the molecular diffusion in the porous phase of the material. By analogy the diffusivity factor of the solid phase could also be used to describe other transport phenomena such as electronic transport, ionic transport, or heat conduction in the solid phase [46].

The tortuosity is determined by the ratio of the path along some particular contiguous phase that exists in a given structure going from some arbitrary points, A and B, in a given sample volume to the straight-line distance between the points A and B. This calculation may seem simple when considering these lengths, but in reality, the determination of the phase path lengths presents a complex problem. In reality, the path existing in a given phase of material is 3D, can have multiple contiguous paths, dead-ends, and multiple cross-sectional areas along a given phase path. All these complexities contribute to the correlation of tortuosity to transport phenomena, but due to the complexity of the calculation, simplifications have been made to approximate these paths. For the tortuosity calculations herein a finite difference discretization method is used to obtain the solution to Laplace’s equation for a quantity of interest, $\phi$, in some homogenous structure. Note that this homogeneous structure could be a homogenous part of a heterogenous structure, i.e. a single phase segmented from a multi-phase structure. Through this solution, the distribution of $\phi$ is determined throughout the homogenous...
structure. This distribution is used to determine the diffusivity property, $D$, for the porous structure, which describes the ability of the structure to transport the quantity of interest ($\phi$). The tortuosity factor, $\psi$, can then be determined by comparing the diffusivity property calculated for the porous structure to the diffusivity of the structure if it was a completely solid. This tortuosity factor is calculated for each of the principal directions of the sample (x, y, and z directions of a Cartesian coordinate system) [34]. An alternative method for calculating tortuosity is the TauFactor algorithm. This algorithm employs an iterative scheme with Over Relaxation (OR) that allows for significant acceleration in convergence [35].

2.4.6 Interfacial Properties

Some useful interfacial properties that can be calculated from 3D reconstructed $\mu$CT images are the three-phase boundary (TPB) line length and the interfacial area between two phases. These two interfacial properties can be of good use in the analysis of microstructural characteristics observed in the research. For example, when two or three constituent phases must be present for a particular chemical reaction to take place, the TPB line lengths and the two-phase interfacial area will quantify the available length or amount of area at which this reaction can occur.

The TPB line length is formed where three constituent phases are present. These TPB line lengths are obtained numerically by using an iterative scheme that goes through each voxel in a given sample, identifying each location that there are three neighboring phases that form the TPB line. This iterative method identifies each of these lines formed and counts the number of voxels that these lines run adjacent to. This number of voxels
that are traversed can then be used with the voxel size to back out the physical length of the TPB lines [46].

To identify the interfacial area between two phases, a similar iterative scheme is used. However, this iterative scheme goes through each voxel in a given image and identifies all locations that two phases of voxels are adjacent to each other and counts the number of voxels at these locations. The number of voxels of a specific phase that are adjacent to voxels of another specific phase are used, along with the voxel size, to back out the two-phase interfacial area of two specific phases. This scheme is executed to determine the area at each of these two-phase interfaces and is done for the interfaces between each phase of interest [46].

In general, these two measures can quantify the available specific surface area for electrochemical reactions. However, the TPB line length is more relevant for fuel cell applications and is not commonly used in battery analysis. Specific interfacial surface area is of interest for battery electrodes and is therefore emphasized in later analyses [46].
CHAPTER 3:  
Methodology

3.1 Microtomography Sample Set  

In order to observe and quantify the microstructural effects of lithiation and delithiation, electrode pellet samples were fabricated, cycled, and then X-ray μCT was performed on the pellet samples. Synthesis of Cu₆Sn₅ pellet electrodes was performed following the methods of Kepler et al. [26]. Further details of the alloy synthesis, X-ray diffraction (XRD), and electrode fabrication are given in Ausderau et al. [27]. A significant majority of the pellet electrodes were found to be Cu₆Sn₅ with smaller amounts of Cu₃Sn, Sn, and Cu. No significant quantities of Sn or Cu oxides were observed. For electrochemical testing pellet electrodes 13 mm in diameter and 1 mm thick were produced. Lithiation and cycling was performed on these electrodes to observe the structural effects of electrochemical cycling. Cu₆Sn₅ pellets were used as the working electrode in a half cell assembled in an argon-filled glove box. These cells included a lithium foil counter electrode and glass fiber separator along with ~200µL of 1M LiPF₆ in diethyl carbonate (DEC) as an electrolyte. Lithiation and delithiation was performed in two voltage windows 0.2-1.5 V vs. Li/Li⁺ and 0-1.5 V vs. Li/Li⁺. The 0.2 V and 0 V were chosen to initiate particular chemical reactions that make up the lithiation/delithiation mechanism. To permit more extensive lithiation of the pellet electrode surfaces the lithiated samples were held at their respective lower voltage limits. Details of the electrode testing and more information behind the voltage choices have been provided by Ausderau et al. [27].
To better understand the coupling of microstructural changes and cycling for alloy anodes a combined electrochemical and μCT study was performed. Galvanostatic lithiation and delithiation was performed on Cu₆Sn₅ pellet electrodes. After cycling, the half cells were disassembled in a controlled atmosphere glove box (~1 ppm H₂O). The surfaces of the Cu₆Sn₅ pellets exhibited a black coating along the exterior surface adjacent to the separator, suggesting lithiation of that surface [19]. This reacted layer was removed from a portion of the pellets for use in nanoscale X-ray imaging [27]. Synchrotron-based X-ray μCT was also performed on larger samples extracted from the pellet electrodes prior to surface layer removal. These μCT samples retrieved from the pellets cycled at the conditions described in Figure 3.1 were placed in plastic pipette tips and cast in epoxy prior to imaging. X-ray imaging was performed at a resolution of 1.3 μm (0.65 μm pixel size) using beamline 2-BM-A at the Argonne National Laboratory Advanced Photon Source (APS). The μCT scans were performed in white beam mode with an exposure time of 50 ms per projection image. Each tomographic scan contained 1500 projection images equally spaced over 180° of rotation.

Prior to analysis, the transmission images were normalized, filtered, and reconstructed into 3D image stacks using a filtered back projection algorithm within the TomoPy software [53]. Once the 3D image stacks were reconstructed, 2 sample image stacks were used from each cycling condition. From these 3D image stacks smaller sample regions were taken and treated as individual samples in the proceeding analysis. Preliminary analysis was completed using three 270 x 270 x 270 voxel edge region samples and one 180 x 180 x 180 voxel center region samples from each of the sample images (giving a total of 8 sample regions for each cycling condition). These samples
were used to calculate the continuous phase size distribution and specific surface areas for the microstructure [54]. All other analysis herein was conducted by taking four 180 x 180 x 180 voxel edge region samples and two four 180 x 180 x 180 voxel center region samples from each sample image giving a total of 8 sample edge regions for each cycling condition. The edge regions were used to evaluate the microstructural changes due to cycling, but the center regions were unreacted. The center regions were compared to each other and to the pristine sample to confirm the consistency in the determined properties of the unreacted structure. This came to a total of 60 samples that were used in the characterization analysis. The reason for the smaller volume regions in the latter is to accommodate computational limitations of the code used in determining the tortuosity. Although this volume is smaller, trade studies for comparing the characterization results such as PSD shows that the smaller volume regions are sufficiently large to be a representative volume of the entire sample images.

3.2 Image Segmentation

The projection image data is used to reconstruct a 3D image for each pellet sample that was scanned. A cross section from the reconstructed image of each pellet sample that was scanned and used for the present analysis is shown in Figure 3.1. Where applicable, the cycling conditions are included. These reconstructions of the pellet samples are analyzed to acquire parameters that can describe the microstructure of each sample. Quantifying microstructural parameters from these X-ray images consist of two main processes: segmentation and analysis. The segmentation and analysis processes were carried out primarily with FIJI and MATLAB.
Figure 3. 1: Cross sectional images of each pellet sample and their corresponding cycling conditions. Two samples were extracted from each cycling condition and three representative volumes were extracted from each sample. The pellet samples are referred to as (a.) Sample 7 (b.) Sample 8 (c.) Sample 9 (d.) Sample 10 (e.) Sample 11.
The segmentation process is done to isolate different materials of interest that reside in the pellet samples for later analysis. The method of segmentation used is a strict thresholding process based on grayscale limits informed by the sample image histogram. This thresholding process consists of establishing ranges of gray values that encompass each material of interest and then using these ranges to isolate a specific material of interest during analysis. The most difficult part of the segmentation process is establishing gray value ranges that can accurately encompass a material of interest without being so broad that the range also encompasses materials of other phases. Gray values can be used to isolate individual materials because the gray value of each voxel in the image has a direct correlation to the attenuation of the object at that location. This attenuation is specific to each material, which makes the gray values specific to each material as well.

To establish ranges of gray values for each material of interest, specific regions of the image were isolated for observation. For the purpose of the analysis presented herein, the image can be broken up into three phases: “reactants” to be lithiated (high attenuation solids Cu₆Sn₅ and Sn), “products” of the lithiation process (intermediate attenuation solids including Li₂CuSn, Li₄.₄Sn, and Cu), and the background (low attenuation epoxy and open pore regions). These materials are considered to be the bulk content of the three phases distinguished by thresholding. However, additional compounds may be present including solid electrolyte interphase (SEI) within the lithiated regions and Cu₃Sn and Sn within the reactant regions [27].

To begin establishing the gray value ranges for these three regions, a large area is selected from the image that contains only what is known to be part of the background, as
shown in Figure 3.2a. A histogram is then calculated for this selected region. Typically, since this entire selected region is known to be background, the histogram of the gray values contained in this selection form a well-defined normal distribution. This normal distribution is used to choose a range of gray values that would encompass the distribution of all background voxels. Figure 3.2b shows a histogram that was observed to determine the gray value range for the background region shown in Figure 3.2a. The upper and lower limits for background thresholding are shown as well. It should be noted that the negative values in this histogram data are the result of phase contrast data retrieved from the tomographic reconstruction. Specifically, some of the voids present in the epoxy can be seen in Figure 3.2a (indicated by the red arrows).
Figure 3.2: The segmentation process starts with (a.) definition of a background region and (b.) the calculation of the background histogram. Voids in the epoxy containing the sample are highlighted with red arrows. (c.) The background voxels are removed with a minimum operation and a region of unreacted material is selected. (d.) The histogram of the unreacted region defines the set of voxels representing $\text{Cu}_6\text{Sn}_5$/Sn within the sample.

Every voxel in the image that has a gray value that falls in the range defined in Figure 3.2b is considered to be part of the background and thresholded out with a value of “NaN”. This setting allows the background voxels to not be considered in future histograms that will need to be calculated while preserving the grayscale values of the remaining voxels. At this point, all that remains in the image is solid material since the background voxels have essentially been nulled. A depiction of an image that just contains solid material is shown in Figure 3.2c.
This solid material, as stated earlier, is broken into two phases of interest. In Figure 3.1, it can be seen that for all of the experimental samples other than the pristine samples, the innermost region consists primarily of the reactants that are to be lithiated, while the edge/outermost region of the samples is where most of the products from the lithiation process reside. With this information, a region towards the center of the sample is selected that can be assumed to consist primarily of Cu₆Sn₅ and Sn. An example of a selection of the center of a pellet sample is depicted in Figure 3.2c. A histogram is calculated for all the voxels in this selected region. The histogram of the center region of the sample is considered a left skewed distribution, the left tail of which is believed to be due to imaging artifacts as well as small amounts of materials other than Cu₆Sn₅ and Sn that skew the gray value distribution to the left. These artifacts can include ring artifacts, beam hardening, and phase contrast effects in the tomographic reconstruction. The next step is to establish another range of gray values that just encompass the material consisting of Cu₆Sn₅ and Sn. Establishing the gray values range from this histogram is a bit more complicated than establishing a range from the background data, because this data is skewed, rather than being strictly a normal distribution.

For establishing this range of gray values, it is assumed that the distribution of the material containing Cu₆Sn₅ and Sn in the microtomography to follow the central limit theorem. This assumption is validated by calculating a histogram of the material in the pristine samples of primarily Cu₆Sn₅ and the minor components identified by XRD. As shown in Figure 3.3, a distribution is formed for the pristine sample that is approximately normal and follows the central limit theorem. Furthermore, this pristine sample exhibits a
distribution and mean values comparable to the interior region of interests for the cycled samples, Figure 3.2d.

Figure 3. 3: Histogram of a pristine pellet sample after the background (low attenuation epoxy) and phase contrast data retrieved from the tomographic reconstruction is removed. Note that the upper and lower limits are bounding the range of gray values that are seen in this histogram.

Under the consideration that Cu₆Sn₅ and Sn distribution follows the central limit theorem, the peak of the left skewed distribution is located and said to be the mean of the Cu₆Sn₅ and Sn gray values distribution. Next, an upper limit that will encompass the gray values to the right of the peak is determined. The peak value and upper limit are compared to determine the number (n) of standard deviations (σ) to the right of the peak that will encompass all gray values to the right of the peak. Once this number of standard deviations is determined, a lower limit for the range is established that is symmetric to the upper limit that was established. This process establishes upper and lower limits that are
symmetric about the peak of the distribution. This symmetry then falls in line with the assumption that the gray values containing Cu₆Sn₅ and Sn follow the central limit theorem when unaffected by artifacts, imperfections, and small amounts of foreign material in the microtomography. Figure 3.2d depicts the histogram of the gray values for the region containing primarily Cu₆Sn₅ and Sn with the upper and lower limits established.

With a range of gray values established for the Cu₆Sn₅/Sn regions in the sample, the images can be segmented into the three regions of interest. There is now a range of gray values that encompass the background and a range of gray values that encompass the reactant materials. The remaining unclassified voxels in the image have gray values that fall between these two ranges and are deemed products from the lithiation process.

3.3 Microstructural Analysis

Using the ranges of gray values for each phase of interest, analysis is performed on each individual phase. The six main procedures for analysis that is carried out on each phase are Continuous Phase Size Distribution (CPSD), Phase Size Distribution (PSD), Cumulative Size Distribution (CSD), Surface Area to Volume ratio (Specific Area) calculation, Interface Area calculation, Connectivity calculation, and Tortuosity calculations.
3.3.1 Phase Size Distribution (PSD)

The CPSD, PSD, and CSD analysis are distinct ways of quantifying the phase distribution of a material. For more information on PSD and CSD analysis method, refer to [31].

The Continuous PSD analysis was run using a combination of Matlab and Fortran routines which utilize a ray tracing method on the segmented microstructural images to calculate ray lengths extending across individual pores/particles. These rays can then be related back to the pore/particle size and thus used to derive the Continuous PSD.

3.3.2 Surface Area Analysis

The Surface Area to Volume calculation is started by creating a MATLAB isosurface from the microtomography data that can serve as a detailed 3D spatial representation of the phase of interest. To create this isosurface, the gray value ranges are used to convert the microtomography data into a binary three-dimensional matrix that can visually and mathematically represent the geometry of the material of interest. This three-dimensional matrix is then used to create the isosurface, which uses linear interpolation to create a smooth continuous surface with the three-dimensional binary matrix. The isosurface is defined by a set of triangular facets characterized by face numbers and the related Cartesian coordinates representing the vertices of each triangular facet. In Figure 3.4, an example of two isosurfaces that are used for surface area and volume calculations are shown. The two isosurfaces are representations of the Cu₆Sn₅/Sn Phase (blue) and Li₂CuSn₄/Li₄Sn₆/Cu phase (red) of a sample region of a pellet sample.
Figure 3. 4: Isosurfaces of the Cu$_6$Sn$_5$/Sn phase and the Li$_2$CuSn/Li$_{4.4}$Sn/Cu phase of the cubic sample region 97.5 µm on each side. The Cu$_6$Sn$_5$/Sn phase is shown in blue and Li$_2$CuSn/Li$_{4.4}$Sn/Cu phase is shown in red. This region is from the edge of sample 7.
Once the isosurface is created for a material of interest, the calculations can be made to find the surface area to volume ratio. The calculations consist of calculating the volume that the voxels encompass as well as calculating the surface area of the isosurface. The former is a basic summation of the elements of the binary image matrix elements. The latter is determined by calculating the area \((A_i)\) of each triangular facet \((i)\) in the isosurface based on vectors \((\mathbf{a}_i\) and \(\mathbf{b}_i)\) defined from the vertices of the facet. These facet areas can then be summed to yield the total area for the cubic sample, Equation 1. Once these two calculations have been made, the surface area to volume ratio can be determined.

\[
A_{\text{total}} = \sum_{i=1}^{n} \frac{1}{2} |\mathbf{a}_i \times \mathbf{b}_i| (1)
\]

The interface area calculation is done to calculate the approximate area that exists at the interface of two given phases and takes a different approach to that of the surface area to volume ratio calculation. Additional description of the interfacial area calculations is given in Section 2.4.6. For the interface area \((IA)\) between two homogeneous phases \(g\) and \(h\), an iterative scheme is first used to determine how many voxels \((n)\) of phase \(g\) are adjacent to a voxel of phase \(h\) throughout the sample volume. This total number of voxels, along with the voxel size \((V_s)\) is used to back out the area of a given interface between the two phases using Equation 2 below [32].

\[
IA_{gh} = \sum_{i=1}^{n} V_s \quad (2)
\]
For the purpose herein, the interfacial areas that were considered are the interface areas between the Cu$_6$Sn$_5$/Sn Phase and Li$_2$CuSn./Li$_{1.4}$Sn./Cu phase as well as between the Cu$_6$Sn$_5$/Sn Phase and pore phase. This could give us additional insight on how much free area there is to accommodate excessive amounts of SEI formation as well as how much lithiation products are adjacent to the Cu$_6$Sn$_5$/Sn phase in the anode.

### 3.3.3 Tortuosity

The Tortuosity calculations were also completed using a combination of Matlab and Fortran routines. For this calculation, the segmented morphology is discretized and a finite difference method is used to obtain a one-dimensional solution to Laplace’s equation across the structure in the direction of interest. Since Laplace’s equation is found in the equation describing diffusion through a porous medium, the diffusivity factor is able to be calculated. This diffusivity factor is analogous to the tortuosity factor and thus the tortuosity factor can be calculated with the diffusivity factor and volume fractions of the phase of interest [7].

### 3.3.4 Connectivity

The connectivity analysis was implemented using a combination of Matlab and Fortran routines. These routines, as described in chapter 2, execute a numerical painting scheme labeling all connects voxels of a particular phase of interest within a sample. This value is then compared with the total volume of the phase to determine the fraction of voxels that are connected. The connectivity of each of the 3 phases of interest were calculated for each of the 60 samples.
3.3.5 Characterization Suite Execution

The analysis for the PSD, CSD, Connectivity, Interfacial Area, and Tortuosity was completed using a Matlab characterization suite developed by Grew et al. [7,8]. The PSD was calculated based on the ray tracing (or LBM-based) method described in Section 2.4.3. This method produces a probability distribution function for phase sizes within sample region analyzed. The CSD can be calculated from this distribution by a straightforward integration.

To implement the characterization, a total of 60 samples (4 edge and 2 center sample regions for each of the 10 sample images) was stored in a directory, each sample in its own folder. The characterization suite was originally developed to analyze each of the four characteristics listed on one sample at a time. This can be time consuming and labor intensive since there were a total of 60 sample regions that needed to be analyzed and the tortuosity calculation can be very computationally expensive (8+ hours for one phase in the 180 x 180 x 180 sample regions). In order to mitigate these time and labor factors, an iterative loop was added to the characterization suite that allowed all 60 samples to be analyzed in a continuous run. This automation did away with the need to monitor the characterization runs and allowed for continuous runs. In the characterization suite, the phases (up to 3) that are being characterized, volume region dimensions in number of voxels in each direction, voxel size, and convergence criteria for the tortuosity calculations are required inputs.

Calculations of phase tortuosity values were completed using the Laplace equation solution method described in Section 2.4.5. This method requires definition of
convergence criteria to manage calculations. These convergence criteria are solely used for the tortuosity scheme since this is the only characterization in the suite utilizing a converging iterative scheme. The first of two convergence criteria is the steady state convergence check, which is input as an exponent of 10, so if the input is \(-4\), then the steady state convergence check is \(10^{-4}\). The steady state convergence check is used to compare solution of the Laplace’s equation at any given voxel in the structure to the solution at the previous iteration. Once the difference between the solution of the two iterations is below this steady state convergence check, then the solution has been reached. The other convergence criteria required is the maximum number of iterations. This number limits the number of iterations that the routine will execute in attempts to converge on the solution to the Laplace equation for the microstructure. Convergence for the tortuosity of the Cu6Sn5/Sn for the sample images herein typically occurred before 50,000 iterations.

The connectivity is determined by utilizing a numerical painting scheme, described in Section 2.4.4. This painting scheme determines the fractional amount of volumetrically connected voxels with respect to the total number of voxels in the sample. This is sometimes referred to as contiguity or volumetric connectivity. More information regarding the calculation of the connectivity of a given phase can be found in Grew et al [32].
4.1 Observed Structural Changes

The goal herein is to quantify the changes to the microstructure of the alloy anode samples described in chapter 3. An example of the microstructural changes that are quantified herein can be seen in figure 4.1 below. This figure contains a partial image of the microstructure of sample 10. The unreacted Cu₆Sn₅ phase can be seen towards the center of samples as the lithiation process does not penetrate this far into the samples. Sample 10 was lithiated to 0 V vs. Li/Li⁺ and the reaction products of this lithiation process can be seen on the left of figure 4.1b. The two solid phases are distinguished by the different gray scale value of the image. As seen in figure 4.1, the unreacted Cu₆Sn₅ shows a brighter gray scale value than the lithiated products. These phases distinctions can also be seen from a 3D perspective in figure 4.2. It also can be seen that as one moves from interior to the exterior of the sample the structure become more broken up.

This is visual evidence of the degrading effects due to lithiation. It is this visual evidence that is quantified with the characterization methods herein.
Figure 4. 1: Taken from sample 10 (Figure 3.1d above). (a) Zoomed image of the one of the sample 10 images in the prior figure. (b) A resliced image of the image along the yellow line shown in part a.

Figure 4. 2: (a) Non-segmented 3D gray scale image. (b) A image that has been segmented into its 3 distinct phases.
As described in chapter 3, it was assumed that the gray scale values of the solid phase of the pristine sample would accurately represent the unreacted Cu₆Sn₅ phase for each of the other samples. This would mean that the material properties should be similar for the unreacted regions of all samples. This was evaluated by comparing the CPSD, PSD, Connectivity, Tortuosity, and Interfacial Area of the center samples to the pristine sample. These results showed that for interior regions of samples 9 and 10, the parameters noted were consistent with the pristine sample (sample 11). However, samples 7 and 8 tended to deviate from the results for the pristine sample. This can be attributed to a few factors. First, both sample 7 and sample 8 have sample images that were taken of smaller volumes compared to the other samples, see Figure 3.1. This leads to a deeper penetration of the lithiation processes into the sample and thus there is not an unreacted region at the center of these smaller samples like there is for the other samples. Second, as it was attempted to obtain multiple sample regions of the center regions that were 180 x 180 x 180 voxel in size, it is evident for samples 7 and 8 that some of the reacted regions were captured in some of these sample regions of the center. These captured reacted regions within the sample regions made it no longer an unreacted structure and rather a combination of reacted and unreacted, which caused the results to deviate from that of the pristine sample.

A visual comparison can be made between a pristine and unreacted sample in figure 4.3. In this figure, the breakup and pulverization of the cycled sample can be seen. It is microstructural changes such as this that will be quantified herein.
4.2 Phase Size Distribution

4.2.1 Phase Size Distribution

For the execution of PSD calculations three 270 x 270 x 270 voxel regions are selected along the edge of each pellet sample. This gives a total of six regions that can be analyzed for every set of cycling condition. Once the microtomography data for each pellet has been subjected to the PSD calculation methods noted earlier, results for the PSD can be used to compare and quantify the microstructural changes that have taken place due to the different lithiation and delithiation processes that are involved with the use of this alloy anode.

Regarding the PSD results for the Cu₆Sn₅ phase, some tendencies can be seen of the alloy anode as it undergoes use in a battery. First, from the PSD results, it can be said
that the alloy anodes undergo more severe destructive microstructural changes during the
delithiation process as lithium is extracted from the Cu$_6$Sn$_5$ anode and the supporting
structure contracts. This can be seen by comparing samples 8 and 9, both tested within
the potential window of 0.2-1.5 V vs. Li/Li$^+$, Figure 4.2a.

Since both samples were lithiated to the 0.2 V, the microstructural changes due to
the lithiation process should be the comparable in each case. This would correspond to
the formation of Li$_2$CuSn. From Figure 4.2, it can be seen that the PSD data shows
sample 8 is at a more pulverized state and has a smaller PSD than that of sample 9. This
observation is what draws us to the conclusion that the alloy anode tends to see
destructive microstructural changes during the delithiation process. This same tendency
can also be seen in the PSD data for samples 7 and 10 from Figure 4.2a. This behavior is
also seen for lithiation of Sn-based anodes [28–30].

As stated, there are destructive microstructural changes that are introduced during
the process of delithiation. However, the Cu$_6$Sn$_5$ anodes are also affected by the lithiation
process. When the Cu$_6$Sn$_5$ anodes are lithiated, they undergo volumetric expansion,
which plays a role in the destructive changes that occur during the delithiation process,
but it also causes some microstructural changes in itself. The PSD data suggests that there
is a difference in the severity of destructive microstructural changes that occur depending
on the amount of lithiation that is done with the anode. For instance, sample 10, which
was fully lithiated to 0 V, shows the Cu$_6$Sn$_5$ phase to have a smaller continuous PSD and
to be much more broken up than the Cu$_6$Sn$_5$ phase in sample 9, which was only partially
lithiated to 0.2 V. This comparison can be observed in Figure 4.2a. This decreased PSD
due to lithiation can be seen in the overall solid phase of the pellets as well. The decrease
in PSD for the overall solid phase can be seen in Figure 4.2b. Another possible cause for this decrease in PSD, other than strictly volumetric expansion, can be due to Cu$_6$Sn$_5$ and Sn reacting with Li$^+$ during lithiation and decreasing the amount of Cu$_6$Sn$_5$ and Sn phase in the pellet.
Figure 4. 4: (a.) Phase size distributions of the Cu$_6$Sn$_5$/Sn phase, with a detailed view of $D_{50}$ for each sample (inset), show progressive size reduction with lithiation and delithiation. (b.) PSDs of the general solid phase in the imaged samples show slight expansion of the solid regions on lithiation and contraction on delithiation. A detailed view of $D_{50}$ region for each sample is included (inset).
More examples of this being the case can be seen when samples 7 and 8 are compared. Sample 7 was fully lithiated and only delithiated to 0.2 V, but shows the Cu₆Sn₅ phase at a more pulverized state than that of sample 8, which was lithiated to 0.2 V and delithiated all the way to 1.5 V. These two comparisons help illustrate that the destructive microstructural changes are lessened by limiting the amount lithiation of the anodes. However, this comes with the price of limiting the electrode capacity.

4.1.1 Continuous Phase Size Distribution from Ray Tracing

For the execution of CPSD calculations utilizing the ray tracing scheme, four 180 x 180 x 180 voxel regions are selected along the edge of each pellet sample. This gives a total of 8 edge regions that can be analyzed for every set of cycling condition. The reason for decreasing the total voxel size of the selected regions was to accommodate the Tortuosity calculations that were executed with the same code as the PSD calculations. Once the microtomography data for each pellet has been subjected to the ray tracing CPSD calculation method, similar results for the PSD can be used to compare and quantify the microstructural changes of the pellet samples as was done with the continuous PSD.

When the CPSD results from the ray tracing method are observed, similar conclusions about the effects that cycling conditions have on the Cu₆Sn₅/Sn phase can be drawn as with the PSD results. First, the results show that the anodes undergo more severe pulverization due to being lithiated and delithiated rather than just being lithiated. This can be seen by comparing the area under the curve for sample 8 and sample 9 in Figure 4.3 and also by comparing the mean phase diameter for samples 8 and 9 in Table
4.1. Again, since both of these samples were lithiated to the same potential of 0.2 V vs. Li/Li⁺, the degradation caused by the lithiation should be comparable. This allows us to infer that the more severe pulverized state of sample 8 can be attributed to delithiation.

This same trend can be seen by comparing the CPSD curves and mean phase diameters for samples 7 and sample 10. Both of these samples were lithiated down to 0 V, but sample 7 was delithiated to 0.2 V and resulted in a more pulverized structure than that of sample 10, which was held at 0 V.

![Figure 4.5: The averaged Continuous Phase Diameter of the Cu₆Sn₅/Sn phase is shown for each of the 5 cycling conditions.](image)

*Figure 4.5: The averaged Continuous Phase Diameter of the Cu₆Sn₅/Sn phase is shown for each of the 5 cycling conditions.*
Table 4. 1: The peak and mean Continuous Phase Diameters of the Cu₆Sn₅/Sn phase for each of the 5 cycling conditions. These values are computed for the results shown in Figure 4.3 above.

<table>
<thead>
<tr>
<th></th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Sample 9</th>
<th>Sample 10</th>
<th>Sample 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Phase Diameter</td>
<td>9.307</td>
<td>23.64</td>
<td>33.3</td>
<td>11.95</td>
<td>33.31</td>
</tr>
<tr>
<td>[µm]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean Phase Diameter</td>
<td>43.36</td>
<td>59.45</td>
<td>72.41</td>
<td>51.26</td>
<td>70.62</td>
</tr>
<tr>
<td>[µm]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The same trends described by comparing the mean phase diameters in Table 1 and the curves in Figure 4.3 can also be seen in Figure 4.4. This figure shows the Pore/Phase Size Distribution for each sample relative to the 3 phases that make up the structure. This allows us to see that the largest PSD for all samples, as expected, is the Cu₆Sn₅/Sn phase. The figure also shows the more pulverized samples showing the curve peak farther to the left of the graph, which reflects more pores/particles are smaller in size than if the curve peak was shifted to the right. So, the PSD curve for sample 7 peaks farther to the left than sample 10 and sample 8 peaks farther to the left than sample 9. Figure 4.4i and 4.4j can be compared to the other graphs in Figure 4.4 to see that the Pristine sample has the largest Pore Size Distribution than any of the other samples. This is a result of the volumetric expansion that occurs upon lithiation. It is also seen that the Pore Size Distribution is also affected by the delithiation as the pore phase is at a more pulverized state in sample 7 than in sample 10 and also in sample 8 than in sample 9. This more pulverized pore phase is due to the pulverization of the solid phases, which leads to the decrease in the contiguous path sizes and can restrict transport associated with the pore.
This trend can be seen by comparing Figures 4.4a and 4.4b to Figures 4.4g and 4.4h as well as comparing Figures 4.4c and 4.4d to Figures 4.4e and 4.4f.

Figure 4.6: The averaged Continuous Pore/Phase size distribution and CSD are shown for each of the 5 cycling conditions. (a-b) reflect the results for sample 7, (c-d) reflect the results for sample 8, (e-f) reflect the results for sample 9, (g-h) reflect the results for sample 10.
sample 10, and (i-j) reflect the results for sample 11. Note that there is no PSD or CSD for the \( \text{Li}_2\text{CuSn}, \text{Li}_{4.4}\text{Sn}, \) and Cu phase since it was not lithiated.

4.2 Surface Area Analysis

4.2.1 Specific Surface Area

When the surface area to volume ratio is calculated for each pellet sample, all of the tendencies that were seen from the PSD of the \( \text{Cu}_6\text{Sn}_5/\text{Sn} \) phase are confirmed. The alloy anodes tend to have an increased surface area to volume ratio when they are delithiated as compared to the anodes that were just lithiated. This tendency can be seen by comparing samples 8 and 9 as well as samples 7 and 10. This is another example that the delithiation process introduces destructive microstructural changes in the anodes. The reason that this change in the microstructure is destructive is that the increased surface area can free up area for SEI formation and contribute to a capacity loss in the electrode. This SEI formation reduces the total Li inventory in the battery, which decreases battery performance. The \( \text{Cu}_6\text{Sn}_5 \) anodes also tend to have a higher surface area to volume ratio when they are fully lithiated to 0 V as compared to when they are just partially lithiated to 0.2 V. This increase in surface area to volume ratio can be noticed in the comparison of samples 9 and 10. These comparisons are all of the same comparisons that are made when observing the PSD data. Figure 4.5 shows the normalized results of the surface area to volume ratio calculations. The data for each phase was normalized by the maximum surface area to volume ratio for each phase to provide a clear comparison between phases.
Figure 4. 7: Normalized surface area to volume ratio of the Cu₆Sn₅/Sn phase and the solid phase of each pellet sample.

4.2.2 Interfacial Area

All of the samples were used to calculate the interface area between two pairs of phases in each anode sample. After comparing the results, it was noticed that there were some results that might be considered outliers. These outliers could be due to image artifacts or possible selecting a small region that is much more fractured than the bulk of the structure. In order to mitigate these outliers, Chauvenet’s criterion was used and results that were outside of the 1.87 standard deviation band were considered outliers and
discarded in the results reported. Further details of this calculation can be seen in Appendix A. The interface area was calculated between the Cu₆Sn₅/Sn phase and the Cu, Li₂CuSn, and Li₄.₄Sn (products) phase as well as between the Cu₆Sn₅/Sn phase and the pore phase. When analyzing the interface area results, it is seen that the samples that were lithiated down to 0 V vs. Li/Li⁺ have a smaller amount of Cu₆Sn₅ phase that is exposed to the pore phase than in the samples that were lithiated to 0.2 V vs. Li/Li⁺. This trend can be observed by comparing samples 7 and 10 to samples 8 and 9 in figure 4.6a. Samples 7 and 10 were both initially lithiated to 0 V vs. Li/Li⁺ and samples 8 and 9 were both initially lithiated to 0.2 V vs. Li/Li⁺. One other possible reason that the samples lithiated to 0 V vs. Li/Li⁺ are exposed less to the pore phase is due to the Cu₆Sn₅/Sn phase reacting with Li⁺ during the lithiation process and decreasing the amount of Cu₆Sn₅ and Sn phase in the pellet as well as increasing the amount of Cu, Li₂CuSn, and Li₄.₄Sn (products) phase in the pellet. Next, it can be observed that the samples that were lithiated all the way to 0 V vs. Li/Li⁺ and not delithiated display a lower interface area between the Cu₆Sn₅/Sn phase and the products phase than the samples that were lithiated to just 0.2 V vs. Li/Li⁺ and not delithiated. This trend can be seen by comparing sample 9 to sample 10 in figure 4.6b. Sample 9 was lithiated to 0.2 V vs. Li/Li⁺ and sample 10 was lithiated to 0 V vs. Li/Li⁺. Both samples were held at their respective voltages, but sample 9 showed a higher interface area. Finally, it can be noticed that the delithiation process increases the surface area of the Cu₆Sn₅/Sn phase that is in contact with the products phase in the anode. This can be seen by comparing sample 7 to sample 9 in figure 4.6b. Sample 7 was lithiated down to 0 V vs. Li/Li⁺ and then delithiated to 0.2 V vs. Li/Li⁺ and sample 9 was lithiated to 0.2 V vs. Li/Li⁺ and held. Both sample 7 and 9 have the same final voltage of
0.2 V vs. Li/Li⁺, but it is evident that sample 7 portrays a higher area at the interface between the Cu₆Sn₅/Sn phase and the products phase. This comparison confirms some of the same behaviors observed by the PSD analysis as well as the surface area to volume ratio analysis. The Cu₆Sn₅/Sn phase in sample 7 has a smaller PSD and a higher surface area to volume ratio than in sample 9. The combination of those geometric parameters leads to the conclusion that the Cu₆Sn₅/Sn phase in sample 7 is more disintegrated than in sample 9, which would lead to more available surface area that could be in contact with the reaction products in the anode samples.
Figure 4. 8: (a.) Interface area between the Cu₆Sn₅/Sn phase and the Cu, Li₂CuSn, and Li₄.₄Sn (products) phase for each sample except sample 11 (pristine) due to the absence of the products phase. (b.) Interface area between the Cu₆Sn₅/Sn phase and the pore phase for each sample.
4.1 Transport Network Characterization

4.1.1 Tortuosity

As discussed earlier, the Tortuosity is calculated for by iteratively solving Laplace’s equation for the segmented microstructure of interest. The solver routine used typically converged on a solution before 50,000 iterations. This convergence can be seen in Figure 4.7. The two parameters plotted in the figure are the Empirical Diffusivity Factor, \( \psi \), and the Tortuosity factor, \( \tau^2 \). The Empirical Diffusivity Factor, \( \psi \), is the parameter that is calculated from the equation for diffusion through a porous medium using the solution of the Laplace’s equation.

Figure 4.9: (a.) Empirical Diffusivity Factor, \( \psi \), for the Cu$_6$Sn$_5$/Sn phase in each of the three primary directions. (b.) Tortuosity, \( \tau^2 \), for the Cu$_6$Sn$_5$/Sn phase in each of the three primary directions. Both figures are from a sample region from a sample 7 image.
After comparing the tortuosity results, it was noticed that there were some potential outliers. These outliers could be due to a localized inconsistency with the bulk structure or image artifacts. In order to mitigate these outliers, Chauvenet’s criterion was used and results that were outside of the 1.87 standard deviation band were considered outliers and discarded in the results reported. Further details of this calculation can be seen in Appendix A. When the Tortuosity is calculated for each pellet sample, all of the tendencies that were seen from the PSD of the Cu$_6$Sn$_5$/Sn phase are confirmed once again. The alloy anodes tend to have a higher Tortuosity factor when they are delithiated as compared to the anodes that were just lithiated. This is shown by the fact that sample 8 shows a higher Tortuosity factor than that of sample 9 and sample 7 shows a higher Tortuosity factor than that of sample 10 in figure 4.8. This reaffirms the trends that show the delithiation process introducing destructive microstructural changes in the anodes. The reason that this is a destructive microstructural change is due to the fact that Tortuosity Factor can be correlated with ionic and electronic conductivity, so the decrease in the Tortuosity factor upon delithiation implies a decrease in conductivity of the anode, thus hindering performance. Similar to what was seen in the other results, the anodes also tend to show a higher Tortuosity factor when they are fully lithiated to 0 V as compared to when they are just partially lithiated to 0.2 V. This trend is observed upon the comparison between samples 9 and 10 in figure 4.8. In addition to comparing the tortuosity values for each of the samples, the variation of the values for a given sample can also be useful. The tortuosity values for sample 7, 8, and 10 show a larger standard deviation than those from samples 9 and 11. This variation in tortuosity values suggest a
varying tortuosity throughout the structure which in turn is due to a breakdown of the structure.

Figure 4. 10: The tortuosity of the Cu₆Sn₅/Sn phase in the x, y, and z directions for each of the pellet samples.
4.1.2 Connectivity

The connectivity for each of the 3 phases present in the samples was also calculated to assess the integrity of the transport networks within. The connectivity is solved for in terms of the fraction of voxels that are connected with respect to the total voxels of that phase. After comparing the results, it was noticed that there were potentially some connectivity results that might be considered outliers. These outliers could be due to image artifacts or selecting a small region that is much more fractured than the bulk of the structure. After further evaluation utilizing the Chauvenet’s criterion outlined in Appendix A, it was found that there were no outliers within the sample sets. Further details of this calculation can be seen in Appendix A. Table 4.1 shows the connectivity results for each phase or each sample with any outliers removed.

Table 4. 2: The mean Pore, Lithiated Products, and Cu$_6$Sn$_5$/Sn phase fractional connectivity for each of the 5 cycling conditions.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Sample 9</th>
<th>Sample 10</th>
<th>Sample 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore</td>
<td>.8921</td>
<td>.7909</td>
<td>.7260</td>
<td>.7434</td>
<td>.7494</td>
</tr>
<tr>
<td>Lithiated Products</td>
<td>.9741</td>
<td>.9069</td>
<td>.7899</td>
<td>.9395</td>
<td>N/A</td>
</tr>
<tr>
<td>Cu$_6$Sn$_5$/Sn</td>
<td>.9993</td>
<td>.9991</td>
<td>.9999</td>
<td>.9982</td>
<td>.9999</td>
</tr>
</tbody>
</table>

The connectivity for the Cu$_6$Sn$_5$ phase was found to be very high. Although the connectivity of this phase was very high for all samples, it does not mean that there were not any destructive geometric changes to the structure. The Cu$_6$Sn$_5$ phase experiences multiple geometric changes as discussed earlier, such as a change in PSD, surface area to volume ratio, and interface area. So, even though the connectivity remains relatively high
for all samples, all samples allude to varying transport properties due to the varying geometric characteristics other than connectivity. The high connectivity value of the Cu₆Sn₅ phase between the samples is due to the fact that any contiguous path in the structure is considered connected by the algorithm used for the calculation. This is completely independent of how big that contiguous path is or how tortuous it is, so this results in most samples showing a high connectivity in that solid phase.

When the pore phase connectivity of the anode samples is observed however, multiple trends appear to confirm previous conclusions from the PSD and surface area to volume ratio results. First, it seems that the connectivity of the pore phase is higher in the samples that were delithiated as compared to those that were just lithiated. This trend can be observed by comparing sample 7 to sample 10 as well as sample 8 to sample 9 in figure 4.9. Samples 7 and 10 were both lithiated down to 0 V vs. Li/Li⁺, but sample 7 was then delithiated at 0.2 V vs. Li/Li⁺. Sample 7 shows the highest pore connectivity out of the sample and this is due to the extensive breakup of the solid structure that occur during lithiation and delithiation, which led to a more connected pore phase. Samples 8 and 9 were both lithiated to 0.2 V vs. Li/Li⁺, but sample 8 was then delithiated at 1.4 V vs. Li/Li⁺. These comparisons add to the confirmation that the microstructural changes in the anode samples depend on the delithiation. It can also be seen that the samples lithiated all the way to 0 V vs. Li/Li⁺ and held at constant voltage portray a higher pore connectivity than the samples that were only partially lithiated to 0.2 V vs. Li/Li⁺ and held at constant voltage. This trend can also be seen by comparing sample 9 to sample 10 in Figure 4.9. Sample 9 was lithiated to 0.2 V vs. Li/Li⁺ and sample 10 was lithiated to 0 V vs. Li/Li⁺. Both of the samples were held at their respective voltages for approximately 7 hours, but
sample 10 shows a slightly higher pore connectivity. In general, the lithiated samples show a lower pore connectivity than the delithiated samples. This reduction may result from volumetric expansion on lithiation closing the pore phase. The connectivity variation seen among each individual sample also varies. Sample 7 has the smallest standard deviation in connectivity and sample 10 has the largest. This could be due to the fact that sample 7 undergoes extensive breakup during lithiation and delithiation to connect the pore regions, which results in a lower standard deviation in connectivity. Sample 10 undergoes extensive volumetric expansion, but does not see as much degradation, since it was not delithiated. This results in a mixture of areas that have a high and low pore connectivity, which results in localized connectivity variations that result in a higher standard deviation in connectivity of the sample. The connectivity of the pore phase can be important when referring to the diffusion transport throughout the anode material.
Figure 4.11: Fraction of the connected voxels with respect to the total voxels of the pore phase for each pellet sample.
CHAPTER 5: Conclusion

There is capability for advancement of the electrochemical capacity of lithium ion battery (LIB) electrodes by utilizing tin (Sn) alloy electrodes. These alloy electrodes show great potential for advancing battery performance due to the high capacity of tin. However, the destructive effects of volumetric expansion must be mitigated in order to sustain this high capacity during extended cycling. One of the ways these effects can be mitigated is by alloying Sn with more malleable metals. By forming this active-inactive alloys, the electrode can attempt to accommodate the severe volumetric expansion with a malleable inactive metal such as copper, while retaining some of the high capacity of Sn. Since expansion is mitigated with an inactive metal, there are losses in the potential capacity of the anode. Another way to accommodate the extreme volumetric expansion of Sn is by forming an alloy with another active metal. This active-active approach results in a higher theoretical capacity than the active-inactive alloy, since the secondary metal participates in the lithiation process.

In order to evaluate the effectiveness of this approach, the microstructural changes due to volumetric expansion were produced by conducting lithiation and delithiation tests of Cu₆Sn₅ pellet electrodes. Ex situ X-ray microtomography was performed on these pellet electrodes after electrochemical testing and this microtomography data was used to quantify the microstructural changes that occur during lithiation and delithiation. The microtomography data was segmented into three distinct phases to evaluate certain characteristics of the samples. The calculations that were used to characterize the
microstructural changes are continuous phase size distribution (PSD), surface area to volume ratio, tortuosity, connectivity, and interface area between phases.

When evaluating the PSD of each electrode sample, it can be seen that the electrodes lithiated to 0 V vs Li/Li⁺ and then delithiated to 0.2 V vs. Li/Li⁺ showed the most substantial reduction in overall phase sizes compared to the other samples. This suggests that full lithiation of the Sn present in the alloy electrodes followed by partial delithiation of the Li₄.₄Sn to Li₂CuSn can cause substantial microstructural changes related to volume expansion on lithiation and structural collapse upon delithiation. The electrodes fully lithiated to 0 V vs Li/Li⁺ and not delithiated show a higher overall phase size distribution, including all solid phases, than the pristine sample and the electrode samples that were partially lithiated to 0.2 V vs. Li/Li⁺ and delithiated to 1.5 V vs. Li/Li⁺. The higher overall phase size distribution that is shown by the sample that was fully lithiated and not delithiated is evidence of the significant volumetric expansion of the Cu₆Sn₅ compound due to lithiation. During this process of volumetric expansion, the phase size distribution of the Cu₆Sn₅/Sn phase is shown to decrease as lower attenuation lithiated phases develop. When the volumetric expansion of the lithiated electrode samples and the volumetric contraction of the delithiated electrode sample are considered together, it can be inferred that the microstructural changes that are observed, such as the decrease in phase size distribution of the Cu₆Sn₅/Sn phase, can be attributed to the volumetric expansion and contraction of the compound during the lithiation and delithiation process.

When considering other microstructural characteristics, the tortuosity for the electrodes lithiated to 0 V vs Li/Li⁺ and then delithiated to 0.2 V vs. Li/Li⁺ show the
highest tortuosity factor compared to other samples. This also suggests that full lithiation of the Sn present in the alloy electrodes followed by partial delithiation of the lithiation products can cause substantial microstructural changes related to volume expansion upon lithiation and structural decomposition upon delithiation. The electrodes fully lithiated to 0 V vs Li/Li$^+$ and not delithiated show a lower tortuosity of the Cu$_6$Sn$_5$/Sn phase, than the pristine sample and the electrode samples that were partially lithiated to 0.2 V vs. Li/Li$^+$ and not delithiated. The higher tortuosity that is shown by the electrode that was fully lithiated rather than partially lithiated is evidence of the destructive effects associated with the full lithiation of the alloy. It can be inferred that the increase in tortuosity is caused by the significant volumetric expansion of the electrodes during lithiation.

In addition to evaluating the effects of cycling conditions on tortuosity, other characterization properties are determined and considered. These additional characterization calculations include connectivity and interfacial areas between phases. When the connectivity and interfacial areas are evaluated, it can be seen that the electrode samples lithiated all the way down to 0 V vs Li/Li$^+$ and not delithiated show a lower connectivity in the pore phase and a smaller interfacial area between the Cu$_6$Sn$_5$/Sn and pore phase than the pristine sample and the electrode samples that were partially lithiated to 0.2 V vs. Li/Li$^+$ and delithiated to 1.4 V vs. Li/Li$^+$. These results show that in addition to the mechanical degradation of the electrodes, excessive volume expansion can also influence transport networks in the active material and supporting phases of the electrode. The less pulverized Cu$_6$Sn$_5$ microstructure in some samples may increase battery performance by creating fewer regions of isolated active material and a more streamlined path for the flow of electrons. This smaller surface area to volume ratio can help prevent
formation of SEI and other unwanted compounds that can decrease the amount of Li\(^+\) available for storage in the anode, which has a negative effect on battery performance.

These results give more understanding in why these Cu\(_6\)Sn\(_5\) anodes show signs of fatigue very early into use as a battery anode. It is evident that as the anodes are lithiated, there is significant volumetric expansion that results in material degradation and when the samples are delithiated continue to see degradation. These changes and their negative effects can be seen in both pulverization of the active material and increased tortuosity of the active material. While based on studies the active-inactive alloy Cu\(_6\)Sn\(_5\) for lithium ion battery applications, the insights obtained are expected to be applicable to other alloy electrodes and battery chemistries.

The methodology described herein could be applied to more of the alloys suggested in section 2.3. The methodology supports nano-materials with nano-scaled images. In the realm of other metallic alloys, it would be useful to further explore active-active alloys such as SnSb, Al-Sn, or silicon/carbon composites with the methods described here in.
REFERENCES


Appendix A:

Chauvenet’s Criterion was applied to various data sets to determine and omit outliers from results. Each data point within the set will be evaluated to see if it is within the maximum allowable deviations ($D_{max}$). $D_{max}$ is a value that is determined from a table and is based on the number of samples within a set. The following equation was used for each data point to determine if it was an outlier.

$$D_{max} \geq \frac{|x - \bar{x}|}{s_x}$$

Where $x$ is the value of a particular data point, $\bar{x}$ is the mean of the sample set, and $s_x$ is the standard deviation of the sample set.

The tortuosity and connectivity data sets with outliers are shown below in tables A.1 and A.2 respectively. The outliers that were removed are shown in red. Sample #’s 1-8 form the sample 7 set, sample #’s 9-16 form the sample 8 set, sample #’s 17-24 form the sample 9 set, sample #’s 25-32 form the sample 10 set, sample #’s 33-40 form the sample 11 set.

A. 1: Tortuosity data set for each edge sample region taken and each outlier that was removed highlighted in red.

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A. 2: Interface area between the Cu₆Sn₅/Sn phase and the pore phase for each edge sample as well as interface area between the Cu₆Sn₅/Sn phase and the Cu, Li₂CuSn, and Li₄.₄Sn (products) phase for each edge sample except sample 11 (pristine) due to the absence of the products phase. Outliers are shown in red.

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