Role of Conductive Carbons in Lithium-ion Batteries: A Spectroscopic Investigation

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A dissertation submitted to

The Faculty of
the College of Science of
Northeastern University
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

April 14, 2017

Dissertation directed by
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Acknowledgements

I would first like to express a tremendous amount of gratitude to my advisors, Professor Sanjeev Mukerjee and Dr. Paolina Atanassova, for sticking with me through this long journey. I could not have gotten this far without their help and guidance. I am truly appreciative of their guidance and support.

I would also like to thank the members of my defense committee, Profs. David Budil and Ke Zhang. I appreciate that they both were willing to be a part of my journey, and I am grateful for their efforts in seeing my defense through to the end.

So many people touch your life when you are on a path like this one. The encouragement, pep talks, and well wishes from my friends and co-workers have been a huge lift for me during this time. A big thank you goes to Dr. Lawrence Murphy for supporting me throughout the past several years. Larry was instrumental in getting Cabot Corporation to agree to let me travel down this path. I cannot thank Larry enough for believing in my abilities, and providing encouragement, and sometimes a kick, along the way. He has been a big part of getting me to this point, and for that I am grateful. Dr. Aurelien Dupasquier deserves many thanks from me as well. The fruitful discussions on electrochemistry and equivalent circuit models were a tremendous help to me. He was always willing to spare a few minutes to go over plots or talk about the experiments that were being planned. Dr. Jincheng Xiong has provided nearly constant encouragement, particularly within the last year. He has frequently checked in with me to see how my progress was going. He also helped me with TEM work that was very important to my dissertation. I am very grateful for his efforts.
I would like to thank Tom Dionne for his help with the SEM, and for the occasional discussion about my work. Tom, along with many others, was always willing to listen to me when I needed to get an idea out of my head. Joe Zapasnik was very helpful with my attempts to pretend being an engineer. Without Joe, I would have been stuck many times. He was willing to give up whatever time was needed to get things going in the right direction. I am very thankful for Joe’s contributions to my work. Kevin Girard deserves my thanks as well. Kevin patiently showed me how to use the equipment in the battery laboratory. He was willing to answer questions or just listen to the ideas rolling around in my head. I cannot express how much I appreciate the help Kevin provided.

The encouragement I received from my co-workers has been outstanding. Paul Shimek has been a steady sounding board throughout this process. A lot of frustration was released in my discussions with Paul. A lot of laughter was heard coming from his office as well. I cannot express how important those moments have been to me. The people I spend my workday with have been wonderful throughout this long road. Every time I thought another step would be too much, someone was there to pick me up. I can’t imagine getting through this without the encouragement and positive thoughts shared by my colleagues.

Dr. Michael Lucarelli put me on this path 22 years ago. He believed that I was capable of getting to this point, and he started me down this road. I cannot thank Mike enough. He taught me so much about being a professional. He is the definition of a mentor. I am very thankful for what Mike gave to me.

Finally, my family deserves the most gratitude. My wife, Sarah, and sons, Cameron and Parker, sacrificed time to allow me to get this work completed. The moments I missed can never
be replayed, but they need to know that I could not have gotten anywhere close to this point without their unwavering support and love. I will never be able to repay them for what they have given to this effort, but I will work tirelessly to show them how important they are to my life.

I extend many thanks to Cabot Corporation financial support, and to the department of Chemistry and Chemical Biology at Northeastern University for allowing me to pursue this work.
Abstract of Dissertation

Increasing the energy density of lithium-ion battery systems is at the forefront of the technology improvements needed in both automotive and portable electronics applications. Operation of lithium-ion cathodes at higher positive potentials is one avenue to achieve higher energy density. Increasing the cathode operating potential is challenging due to the detrimental effects higher voltages have on system durability and cycling performance. Conductive additives play an important role in performance of the lithium-ion cathode. Conductive carbon materials are responsible for providing sufficient electrical conductivity to the electrochemically active material in the cathode. Conductive carbon black also minimizes the heat generation within the cell, which reduces detrimental effects on electrolyte stability at increased electrode potential. Unfortunately, the high surface area and surface chemistry of conductive carbon black contributes to the degradation of the electrolyte in the battery cell. High energy density lithium-ion batteries require more stable conductive additives to achieve the safety and longevity necessary for use in automobiles and portable electronics.

The focus of this research was to understand the role carbon black plays in the degradation of the electrolyte in the lithium-ion battery cell at operating voltages at or above 5 V. Thermal treatment of the carbon black was used to alter the surface chemistry and particle structure as a means to improve stability towards electrolyte degradation. The electrochemical performance of the modified carbon black was studied in both a carbon electrode and a more traditional high voltage spinel cathode. The understanding gained in this work will assist in the design of new conductive carbons that provide the needed stability in high energy density lithium-ion batteries.
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Chapter 1 Lithium-ion Batteries and Conductive Carbons

1.1 Renewable Energy

Efforts to reduce the dependency on fossil fuels have been actively pursued for decades. The reduction in greenhouse gas emissions has been a major goal of the reduction or more efficient use of fossil fuels for energy production. Two major efforts to reduce the use of fossil fuels are in the energy sector and the automotive industry. According to the U.S. EPA, the energy sector was responsible for 32% of the greenhouse gas emissions in the United States in 2012\(^1\). Figure 1.1 shows the impact of CO\(_2\) emissions by economic sector. Electrical energy and transportation are the top two producers of greenhouse gases. Industry accounts for the next largest contribution to greenhouse gases. Efforts in carbon capture and sequestration have been moving forward in the industrial and electricity sectors\(^2\). The carbon capture is expected to significantly reduce the contribution of CO\(_2\) and other greenhouse gases to the environment. The use of redox flow batteries\(^3\) for grid storage facilities to harvest energy from solar and wind applications is under investigation. Lead acid batteries make up about 17% of the grid energy storage\(^4\), but lead acid is also being targeted for use in mild hybrid electric vehicles. Lithium ion batteries have taken over the energy storage landscape, particularly for automotive applications.
Figure 1.1 Greenhouse gas emissions for the United States in 2012 by sector (http://www.epa.gov)

The development of batteries for the electric vehicle has been a major source of research effort for a few decades. Although battery powered automobiles can be traced back a century, the focus on development of electric vehicle (EV) technologies has been at the forefront of the science community for the past two decades. The amount of energy available from a battery, and how quickly that energy can be utilized or stored are both very important qualities in evaluating battery technology. The safety aspects of the battery system are very important to the widespread use of batteries particularly in applications that require high charge and discharge rates. The basic function of the lithium ion battery along with potential degradation mechanisms would be instructive to review.
1.2 Lithium-ion Batteries Basics

The lithium ion battery is made up of a cathode which consists typically of a transition metal oxide material and a graphite anode. During charging, lithium ions move from the cathode through the electrolyte and separator to the anode. The lithium ions intercalate into the layered structure of the graphite anode. Oxidation of the cathode material during charging generates an electron that moves in an external circuit to the anode. Upon discharge, the lithium ions move back towards the cathode while electrons flow as current in the external circuit back to the cathode.

![Illustration of a typical lithium ion battery cell](image)

Figure 1.2 Illustration of a typical lithium ion battery cell

An example of the redox reactions that occur in a lithium ion battery are given below for LiCoO$_2$ cathode material.

\[
\text{C} + \text{LiMO}_2 \xrightarrow{\text{charge}} \text{Li}_{x-\text{Li}}\text{MO}_2 + \text{Li}_x\text{C}
\]
Many different forms of cathode materials exist for lithium ion batteries. The illustration given in Figure 1.3 provides an overview of some of the chemistries available for both cathodes and anodes. The available anode materials have much higher capacity than the cathode materials. Cathode materials have been the focus of many research efforts in an attempt to increase the capacity to match the anode materials. At this point, the cathode materials continue to limit the overall power and energy available from the lithium ion battery.

Figure 1.3 Ragone plot of various cathode and anode options for lithium ion batteries

Scheme 1.1 Example of lithium cobalt oxide oxygen reduction equation for charge cycle of lithium ion battery

\[
\text{LiCoO}_2 + yC \rightarrow \text{Li}_x\text{C}_y + \text{Li}_{1-x}\text{CoO}_2 + e^-\\
\text{Co}^{3+} \rightarrow \text{Co}^{4+} + e^-
\]
The battery cell is designed such that it can withstand thousands of charge and discharge cycles. When damage occurs to the battery, performance can be compromised, sometimes with severe consequences.

1.3 Battery Failure Mechanisms

A brief overview of the failure modes for lithium ion batteries will provide context for the work described in this thesis. Failure modes in lithium-ion batteries result in a variety of outcomes ranging from the inconvenient to the catastrophic. The loss of capacity in a battery registers on the level of inconvenience. However, capacity loss may be a sign that side reactions are occurring in the battery cell that could lead to a more catastrophic failure.

Common failure modes can be separated into external and internal groups. External failure modes include, but are not limited to, problems with design, overcharge or over-discharge of battery cells, or external damage to the cell. Internal failures may be related to a failure of the separator\textsuperscript{7-8}, lithium dendrite growth\textsuperscript{9-10}, degradation of the electrolyte\textsuperscript{11-14}, or structural distortion of the electrode\textsuperscript{15}.

Separator failure can be the result of poor material quality or external damage to the cell\textsuperscript{7-8}. When the integrity of the separator is poor, that allows for direct contact to be established between the cathode and anode. An internal short circuit would result which could also lead to thermal runaway in the cell. Separator failure can result in severe consequences in terms of safety.

Dendrite growth is a major concern for alternative anode materials that operate at potentials that are near the formation of lithium metal. At low potentials, lithium dendrites
deposit on the surfaces of the anode, and the dendrites continue to grow as the battery undergoes charge and discharge. Eventually, the dendritic formations pierce the separator creating a short circuit situation.

Degradation of the electrolyte is the topic of interest in terms of this project. The high surface area of carbon black, coupled with the presence of oxygen containing functionality, can play a significant role in electrolyte degradation reactions. Reduction of electrolytes at the graphite anode in a lithium ion battery has been studied by Aurbach et al\textsuperscript{14, 16-17}. The oxidation of electrolytes at the cathode has also been studied\textsuperscript{13, 18}. The role carbon plays in reactions at the cathode surface is the primary goal of this work.

1.4 Electrolytes

The transport of Li\textsuperscript{+} cations from one electrode to the other in a lithium-ion battery is critical for successful charge-discharge behavior. During charging, lithium ions move from the cathode to the anode, while an electron moves in the external circuit. The reverse process occurs upon discharge. The electrolyte used in the battery provides the means for ions to shuttle from one electrode to the other inside the cell. The choice of salts, solvents, and additives in the electrolyte can have a big impact on safety and performance of the battery cell.

Three important attributes of the electrolyte are the ionic conductivity, the solubility of the lithium salt, and the safe range of operating potentials for the salt and solvent. Fast charge and discharge rates require high ionic conductivity to facilitate movement of ions between electrodes rapidly. The lithium salt chosen will impact the diffusion or movement of Li\textsuperscript{+} in the bulk solution. The solubility of the lithium salt in the solvent system is highly important as well.
The operation of the battery cell is dependent on the availability of Li+ to move from the cathode to the anode through the bulk solution. Loss of capacity or slow charge/discharge rates would result from poor solubility. Internal resistance may generate heat in the battery from the lack of ions in the electrolyte solution as well. Additional safety concerns arise from the stability of the electrolyte at high operating potentials. Increasing demands for high power batteries are pushing the operating potential of cathodes to 5 V and beyond. It is critical to ensure that the chosen electrolyte has the appropriate stability at high voltages. Oxidation and reduction of solvents have been studied using a variety of salt and solvent combinations. No combination of lithium salts and solvents solves all of the challenges of high voltage operation in the lithium-ion battery, but a balance can be found to provide reasonable stability without sacrificing conductivity in the cell. The formation of stable layers at each electrode surface is important for long battery life as well. The solid-electrolyte interface (SEI) layer has been studied for both anodes and cathodes.

1.5 Conductive Carbon Additives

Currently, conductive carbon black makes up a majority of the additive to the commercial cathodes used in lithium ion batteries. Graphenes and carbon nanotubes are being investigated as alternatives to carbon black as a conductive additive to take advantage of the unique properties of each material. Carbon black is the material of interest in this study.

Carbon black is an inexpensive powder that provides conductivity to the mainly insulating cathode. Carbon black is responsible for a majority of the surface area in the cathode even though, for some applications, the carbon black accounts for approximately 10% of the mass of the cathode. One practical issue with the use of carbon black is that it provides no useful
electrochemical performance. Effectively, the mass of the carbon black used in the electrode is kept to a minimum to save space for more active material. The energy density of the battery suffers as the mass of carbon black increases in the electrode. Ultimately, new carbon black materials that provide high conductivity and establish the percolation network at a low mass in the electrode are desirable. Surface chemistry and structure are important features for the ideal carbon black. In order to propose new carbon blacks for use in lithium ion batteries, an understanding of how carbon black participates in the degradation of battery performance.

12. Tarascon, J. M.; Guyomard, D., New Electrolyte Compositions Stable Over the 0 to 5 V Voltage Range and Compatible with the Li1+xMn2Ov/carbon Li-ion Cells. Solid State Ionics 1994, 69, 293-305.
13. Yang, L.; Ravdel, B.; Lucht, B. L., Electrolyte Reactions with the Surface of High Voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Cathodes for Lithium-Ion Batteries. *Electrochemical and Solid-State Letters* **2010**, *13* (8), A95.


Chapter 2 Study of Heat Treated Carbon Black

2.1 Introduction

In general, lithium-ion cathode materials are poorly conductive lithium containing transition metal oxide materials such as LiFePO₄, LiCoO₂, and LiMnO₄. Carbon black is added to the metal oxide materials to improve the electrical conductivity in the cathode. Carbon black also provides benefits in terms of rheology control, charge storage, and thermal properties. The electrical conductivity performance is of primary interest in this work. Carbon black is added to the electrode paste along with binder, electrochemically active cathode material, and solvent. The paste making procedure is generally not energetic enough to fully disperse the carbon black particles. In other words, the carbon black structure is not reduced down to the aggregate size. The carbon black particles in the resulting electrode paste likely have a particle size somewhere between the aggregate and agglomerate size range. Carbon black provides a conductive network through the extensive contact points between aggregates when mixed at the proper concentration in the formulation of interest. The percolation threshold is the concentration of carbon black added to the system that allows for long-range connection between aggregates. The percolation threshold for conductivity has been studied for many carbon black filled polymer systems¹⁻⁴. Above the percolation threshold, no further benefit is realized in the conductivity of the material. Below the percolation threshold, the number of contact points between carbon black aggregates is too low to provide much benefit to the overall cathode. The intimate contact between the carbon black and cathode powder highlights the need to understand the impact carbon black has on the performance of the cathode.
The initial goal is to understand how the structure and surface chemistry of carbon black impact the performance of lithium-ion cathodes. The goal of this work was to characterize a series of carbon black samples that were subjected to increasing levels of thermal treatment. The main hypothesis is that heat treatment provides a more stable conductive carbon for use in cathodes operating at high potentials. The source of the stability is thought to arise from the change to a more graphite-like structure. The reduction in oxygen containing functional groups at the edge sites of the carbon black aggregate is thought to contribute to the stability particularly towards electrolyte degradation. Oxygen measurements are not covered as part of this work. Previous work has shown that levels of oxygen are dramatically reduced through thermal treatment of carbon black\textsuperscript{5-6}. The primary techniques used to characterize the samples were X-ray diffraction and Raman micro-spectroscopy. Additional techniques were used to determine physical characteristics of the carbon black powders such as surface area, structure, and particle size.
2.1.1 Structure of Carbon Black

The physical appearance of carbon black on the macro scale is a finely divided black powder or pellet. The specifics of the carbon black formation are beyond the scope of this document, but a high level summary is provided here for context. Carbon black is produced using a high temperature flame process where high boiling polyaromatic feedstock is partially combusted. The resulting powdery substance is collected and further processed for end use.

The three stages of carbon black formation in the flame are nucleation, aggregation, and agglomeration\(^7\). Primary particles are small spherical particles formed as a result of the nucleation stage. During the aggregation stage, primary particles collide together. As collisions continue to occur, primary particles will begin to “stick” to each other forming larger aggregate structures as depicted in Figure 2.2. The primary particles are strongly fused together in the aggregate structure.

*Figure 2.2 Representation of primary particle and aggregate structure of carbon black*
Aggregates will collide much as the primary particles, which ultimately results in larger structures known as agglomerates. The agglomerate structure is not as tightly bound as that of primary particles in the aggregates. The carbon black agglomerate makes up the powder one sees in a container of carbon black. The timescale of the three stages of growth is on the order of 10 ms. The growth of the particles is stopped during the quench stage of the process. The carbon black process provides flexibility to produce aggregate structures of a variety of sizes and shapes. The size and arrangement of the primary particles in the aggregate structure are dependent on the conditions of the flame process. For example, the aggregate structures shown in Figure 2.3 represent a low and high structure carbon black. The primary particles are different sizes, and the branching of the primary particles is very different in the two aggregates. The nature of the primary particle size, degree of branching, and surface chemistry of the aggregate give the carbon black the desirable properties (e.g. rheology, reinforcement, conductivity, etc.).
Figure 2.3 Example of high and low structure carbon black aggregates, (a) low structure aggregate with large primary particle size and very little branching, (b) high structure aggregate with small primary particles and extensive branching in the aggregate.

2.1.2 Carbon Black Crystallite Size

The arrangement of carbon atoms in the primary particle of carbon black is similar to that of graphite. The unit cell of graphite is shown in Figure 2.4. A collection of carbon layers, much like graphene sheets, make up regions of short-range ordered carbon\textsuperscript{8}. Although the arrangement of carbon atoms is similar to that of graphite, carbon black differs due to the rotations of the carbon “sheets”, dislocations, and other defects that limit the crystallite size. The term crystallite size is not strictly correct when referring to carbon black. However, the term crystallite size has been adopted in the literature to describe the structural order present in the carbon black primary particle\textsuperscript{8-10}. The spacing between the carbon sheets is another difference between carbon black and graphite. Carbon black layer spacing is larger than that observed for
graphite. The size of the short range ordered domains in carbon black can be estimated from X-ray diffraction and Raman measurements.

![Illustration of graphite unit cell](image)

**Figure 2.4** Illustration of graphite unit cell

The crystallite size of carbon black particles is typically defined in both the \(a\)- and \(c\)- directions. As shown in Figure 2, the \(c\) direction is perpendicular to the carbon basal plane. The crystallite grows by the addition or organization of layers perpendicular to the basal plane. The value of \(L_c\) can be thought of as the stacking height of the crystallite. For graphene materials, the spacing between layers, \(d\), is used to calculate the numbers of layers contained in the crystallite. A
similar approach can be taken for carbon black. The crystallite size in the $a$-direction is an estimation of the diameter of the crystallite. Lateral growth is measured in the $a$-direction using either x-ray diffraction or Raman spectroscopy. Growth in the $b$-direction would be equivalent to the $a$-direction since both lie in the same plane. Hence, $La$ is the measurement referenced in the literature. Thermal treatment of carbon black results in growth of the crystallite in both the $a$- and $c$-directions. The characterization of the carbon black crystallite was done using both $La$ and $Lc$.

2.2 Experimental

2.2.1 X-Ray Diffraction

X-ray diffraction patterns were collected using a PANalytical X’Pert Pro diffractometer equipped with a 1.8 kW X-ray tube using a Cu target. Diffraction patterns were collected over a range of 2-theta values from 8 to 90 degree using Bragg-Brentano geometry. Line broadening due to the instrument is corrected using the pattern from a lanthanum hexaboride standard, $LaB_6$. Peak fitting was completed using the HighScore software package.

2.2.2 Raman Micro-spectroscopy

Raman spectra were collected using a Horiba LabRAM Aramis Raman microscope. A 100mW 532 nm laser was used for the carbon black measurements. A notch filter was utilized to reduce the laser power to 1 mW (1%) of maximum in order to avoid heating the sample during analysis. The laser was focused on the sample surface through an Olympus 100X objective (NA = 0.9, WD = 0.21mm).
Samples of carbon black were applied in a thin layer onto a double-sided adhesive tape supported by a microscope slide. Five spectra were collected over an area of approximately 25 mm$^2$ to evaluate the heterogeneity in the carbon black sample.

Curve fitting procedures were completed using the LabSpec6 software package. Baseline correction and corrections due to the notch filter were executed on each spectrum collected.

2.3 Results and Discussion

2.3.1 X-Ray Diffraction Analysis of Carbon Black

![Graph](image)

**Figure 2.5** Amorphous Carbon Black Diffraction Pattern

The carbon black diffraction pattern has several features of interest for the characterization of the crystallite. A typical diffraction pattern of untreated carbon black is shown in Figure 2.4. The most prominent feature is the (002) reflection at approximately 20
=25°. Additional reflections, (100) and (110), are present in the diffraction pattern at approximately 43° and 78° respectively.

The (100) and (110) features are broad peaks with low intensity. The (100) reflection is used to estimate \( L_a \) while the more intense (002) reflection is used to estimate the value of \( L_c \). The crystallite size is determined using the peak fitting capabilities in the HighScore software package for X’Pert Pro instrument. The peak position, 2\( \theta \), and the peak width at half of the maximum intensity (FWHM) are determined through the peak fitting manipulations. The crystallite size is calculated using equation 2.1,

\[
L (\text{Å}) = \frac{K\lambda}{\beta \cos \theta}
\]  

(2.1)

where \( K \) is a shape factor set to 1.0, \( \lambda \) is the x-ray wavelength, 1.54056 Å, \( \beta \) is the FWHM value, and \( \theta \) is the Bragg angle in degrees. In order to provide the best estimation of the ordered crystalline domain, peak asymmetry must be properly handled when fitting the diffraction peaks. Peak fitting for the (100) reflection is challenging due to the asymmetry of the peak. Additional peaks for the (101), (102), and the (004) reflection are present in the region with (100)\(^{11}\) which contributes to the difficulty in fitting the peak shape. The additional reflections are lost in the background for carbons with higher amorphous content. As the carbon becomes more ordered, additional peaks grow out of the baseline of the diffraction pattern.

The layer spacing in the carbon black structure can be determined using Bragg’s Law shown in equation 2.2,

\[
n\lambda = 2dsin\theta
\]  

(2.2)
where $n$ is a positive integer, $\lambda$ is the x-ray wavelength, $d$ is the layer spacing, and $\theta$ is the Bragg angle. From equation 2.2 it can be seen that the layer spacing and Bragg angle are inversely proportional. In other words, peak shifting to higher angles correlates to a decrease in layer spacing.

### 2.3.2 Impact of Heat Treatment on $L_c$ of Carbon Black

A series of samples were prepared from an unmodified carbon black base material. The details of the reactor design and reaction parameters are of a proprietary nature. The parameter of interest for the series of carbon black samples is the temperature of reaction. The temperature of reaction has been transformed to a relative temperature for the purpose of the work described in this document. The carbons were held at the specified temperatures to allow conversion of the amorphous phases of the particles to a more ordered graphite-like structure. Kinetic growth information cannot be gleaned from the series of carbons described here. The timescale necessary to understand the kinetic growth parameters is orders of magnitude less than what was experienced by the samples in this work.
Figure 2.6 XRD patterns of heat treatment series of carbon black

Figure 2.5 shows the XRD patterns for the series of heat treated carbon blacks, denoted CB1 through CB6. The narrowing of the (002) peak as temperature increases is observed in the overlay of the diffraction patterns. The (002) band shifts to higher 2θ angles as the temperature increases as well. The decrease in the FWHM value results in larger calculated crystallite sizes in the c-direction as per equation 2.1. As the treatment temperature increases, additional layers of carbon are organized in the primary particle resulting in a larger stacking height. In addition, heat treatment of the carbon black causes the layer spacing to approach that of graphite. A shift to higher angles of the (002) peak corresponds to the decrease in layer spacing as determined by equation 2.2.
Growth in the a-direction is observed with the narrowing of the (100) peak in the diffraction pattern. Overall, the observed peaks tend to increase in intensity and decrease in peak width as the carbon materials experience higher temperature environments. The (004) peak becomes easily distinguishable from the background for CB5 and CB6. The crystallite sizes of the carbon black series (CB1 to CB6), as determined by X-ray diffraction, are provided in Table 2.1. The results in Table 1 include the layer spacing, d, and the estimated number of layers in each crystallite, n.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>(002)</th>
<th>(100)</th>
<th>d_{002} (Å)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB1</td>
<td>15.3</td>
<td>18.6</td>
<td>3.585</td>
<td>4</td>
</tr>
<tr>
<td>CB2</td>
<td>20.7</td>
<td>21.6</td>
<td>3.534</td>
<td>6</td>
</tr>
<tr>
<td>CB3</td>
<td>25.9</td>
<td>23.3</td>
<td>3.504</td>
<td>7</td>
</tr>
<tr>
<td>CB4</td>
<td>29.6</td>
<td>25.5</td>
<td>3.489</td>
<td>8</td>
</tr>
<tr>
<td>CB5</td>
<td>32.2</td>
<td>30.7</td>
<td>3.479</td>
<td>9</td>
</tr>
<tr>
<td>CB6</td>
<td>42.7</td>
<td>43.8</td>
<td>3.461</td>
<td>12</td>
</tr>
<tr>
<td>Denka</td>
<td>29.6</td>
<td></td>
<td>3.501</td>
<td>8</td>
</tr>
<tr>
<td>Super P</td>
<td>19.7</td>
<td></td>
<td>3.568</td>
<td>6</td>
</tr>
</tbody>
</table>

Further indication of the increased ordering of the carbon black samples can be seen in the d-spacing values. The d-spacing approaches that of graphite, 3.354 Å as the treatment temperature...
increases. Results for Denka and Super P carbon black samples were included to provide a reference to conductive carbons used in lithium ion battery systems.

2.3.3 Comparison of \( L_a \) Measured by X-Ray Diffraction and Raman Micro-spectroscopy

Raman micro-spectroscopy is used to estimate the carbon black crystallite diameters. The work by Tuinstra and Koenig\(^{12}\) on graphite demonstrated that the relationship between the graphitic and disordered carbon bands in carbon materials could be used to estimate the diameter, \( L_a \). Many studies on the nature of carbon materials using Raman spectroscopy have been completed over the past 4 decades\(^{10,13-19}\).

First, the relationship between the values of \( L_a \) determined from x-ray studies needs to be evaluated versus the Raman micro-spectroscopy measurements. Replicate Raman spectra of each carbon black in the thermal treatment series were collected. In Tuinstra and Koenig’s original paper\(^{12}\), the ratio of the intensities for the D and G band in the Raman spectra were related to the crystallite size using equation 2.3,

\[
\frac{I_D}{I_G} = 4.35 \times \frac{1}{L_a} \quad (2.3)
\]

\[
L_a = 43.5 \times \frac{A_G}{A_D} \quad (2.4)
\]

where \( L_a \) is the crystallite size in nm, \( I_D \) is the intensity of the D-band at 1340 cm\(^{-1}\), and \( I_G \) is the intensity of the G band at 1540 cm\(^{-1}\). Peak area, \( A_D/A_G \), was substituted for peak intensity for this work, and the coefficient of equation 2.3 was multiplied by a factor of ten to convert \( L_a \) into
units of angstroms as in equation 2.4. The plot of the $L_a$ by x-ray diffraction versus the inverse of the area ratio, $A_G/A_D$, is shown in Figure 2.6. A statistically significant linear relationship exists between the $L_a$ measurement from x-ray diffraction and the ratio of the G band area to the D band area. The slope of the linear regression equation was 43.3 which is in good agreement with that of previously reported studies of carbon materials using the peak intensity in the Raman spectrum$^{12, 20}$. Based on the results of the regression analysis shown in Table 2.2, it was determined the Raman analysis was appropriate for the study of carbon black samples.

![Figure 2.7 Linear regression of $L_a$ from x-ray diffraction versus the area ratio of the G to D band in the Raman spectrum using 532nm excitation laser source. (Dashed line represents 95% prediction interval; Shaded region represents 95% confidence interval)]](image)

The Raman analysis has operational benefits in terms of sample preparation and sensitivity towards carbon black versus x-ray diffraction. Specifically, the 532 nm excitation laser used for
Raman analysis is estimated to penetrate the sample to a depth of less than 1 μm. The surface of the carbon sample is sampled more so than the bulk of the sample when using Raman spectroscopy. X-ray diffraction, by contrast, is a measurement of the bulk average of the sample since the x-rays penetrate through the entire depth of the carbon sample. Based on the regression analysis, the measurement of \( L_a \) using the Raman microscope is suitable for carbon black.

### Table 2.2 ANOVA Regression Statistics for Plot of \( L_a \) vs \( A_G/A_D \)

<table>
<thead>
<tr>
<th>Linear Fit</th>
<th>( L_a ) (XRD) = 0.4451567 + 43.301724*( I(G)/I(D) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary of Fit</td>
<td></td>
</tr>
<tr>
<td>RSquare</td>
<td>0.984463</td>
</tr>
<tr>
<td>RSquare Adj</td>
<td>0.982909</td>
</tr>
<tr>
<td>Root Mean Square</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>1.296843</td>
</tr>
<tr>
<td>Mean of Response</td>
<td></td>
</tr>
<tr>
<td>Observations (or Sum Wgts)</td>
<td>12</td>
</tr>
<tr>
<td>Analysis of Variance</td>
<td></td>
</tr>
<tr>
<td>Source</td>
<td>DF</td>
</tr>
<tr>
<td>Model</td>
<td>1</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
</tr>
<tr>
<td>C. Total</td>
<td>11</td>
</tr>
</tbody>
</table>

2.3.4 Impact of Heat Treatment on \( L_a \) of Carbon Black

The Raman spectrum of carbon black shows both first and second order features. The calculation of crystallite size, \( L_a \), involves the use of the first order spectral features between 1000 cm\(^{-1}\) and 1800 cm\(^{-1}\). The Raman spectrum of an unmodified carbon black is shown in
Figure 2.7a. The first order spectral features are of particular interest in determining the crystallite diameter of carbon black. Peaks centered at 1340 cm\(^{-1}\) and 1580 cm\(^{-1}\) correspond to the disordered and graphitic carbon bands respectively. Three additional bands are present in the region along with the D- and G- bands (D*, D**, D’) as shown in Figure 2.7b. The nature of the D*, D**, and D’ bands has been discussed in several research efforts focused on carbonaceous materials such as soot\(^{21}\), graphite\(^{12, 17, 22}\), graphene oxide\(^{16, 18, 23}\), and carbon black\(^{24-25}\). The D bands are all thought to be related to disorder or defects in the carbon sheets.
Figure 2.8 Raman spectrum of a) untreated carbon black, b) Gaussian + Lorentzian peak fit of carbon black Raman spectrum

Curve fitting is necessary to obtain the area of each of the bands in the first order spectrum. The peaks are fit using a combination of a Gaussian and a Lorentzian curve. In Figure 2.7b, the peak fitting of the untreated carbon black sample is shown. Changes to peak shape and intensity in the Raman spectrum are observed as carbon black is exposed to increasing levels of thermal treatment. Increased levels of temperature result in a decrease in width of the
D-band, but a slight increase in the intensity of the D-band is observed with increasing crystallite size. The G-band experiences an increase in intensity and decrease in FWHM as the treatment temperature increases. The spectra of the thermally treated series of carbon blacks are shown in Figure 2.8. The average FWHM values obtained from carbon black Raman spectra are given in Table 2.3. The FWHM values for D*, D**, and D’ show no discernible trend with respect to thermal treatment temperature. The FWHM values for the D- and G-bands both decrease as the treatment temperature increases, but the FWHM for the D-band behaves differently from the G-band with respect to crystallite size. A plot of the D-band FWHM shows a statistically significant relationship with the reciprocal of crystallite size for both La and Lc. By contrast, the G-band shows a linear decrease versus the crystallite size for the thermal treatment series. The difference in the regression of D and G versus crystallite size indicates separate mechanisms for the loss of the short range ordered domains and growth of the graphitic regions in the carbon black samples. The FWHM comparison to crystallite size is shown in Figure 2.9 (a-d). The crystallite diameter was calculated for each of the thermally treated carbon black samples using equation 4. The values for L_a calculated from Raman analysis are given in Table 2.4 along with the L_a and L_c measurements from x-ray diffraction measurements. Relative standard deviations are given in Table 2.4 for each measurement technique.
Table 2.3 FWHM from Raman Spectral Peak Fitting for Heat Treated Carbon Black

<table>
<thead>
<tr>
<th>Carbon</th>
<th>D*</th>
<th>D</th>
<th>D**</th>
<th>G</th>
<th>D'</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB1</td>
<td>186</td>
<td>139</td>
<td>175</td>
<td>75.7</td>
<td>31.9</td>
</tr>
<tr>
<td>CB2</td>
<td>275</td>
<td>104</td>
<td>155</td>
<td>79.0</td>
<td>-</td>
</tr>
<tr>
<td>CB3</td>
<td>218</td>
<td>85</td>
<td>145</td>
<td>71.5</td>
<td>63.6</td>
</tr>
<tr>
<td>CB4</td>
<td>290</td>
<td>70</td>
<td>134</td>
<td>67.5</td>
<td>40.0</td>
</tr>
<tr>
<td>CB5</td>
<td>271</td>
<td>59</td>
<td>211</td>
<td>57.3</td>
<td>33.9</td>
</tr>
<tr>
<td>CB6</td>
<td>224</td>
<td>60</td>
<td>203</td>
<td>52.1</td>
<td>34.7</td>
</tr>
</tbody>
</table>

Figure 2.9 Raman spectra collected for heat treated carbon black samples a) base carbon black not heat treated, b)-f) carbon black samples in order of increasing treatment temperature
Ungar et al.\textsuperscript{10} proposed estimating the amorphous content of the carbon black materials using the integrated intensity of the D** peak divided by the total area of the region between 1000 cm\textsuperscript{-1} and 2000 cm\textsuperscript{-1}. The D** peak downward shift in position as the carbon black crystallite size increased. The peak width was not well correlated to treatment temperature or crystallite size, therefore estimation of the amorphous content using the D** peak was not deemed appropriate for this study. The position and intensity changes in both the D* and D’ peaks likewise did not show a statistically significant relationship with either treatment temperature or crystallite size. The results of the Raman analysis focused mainly on the behavior of the D- and G-band.

![Graphs](image_url)

**Figure 2.10** Regression analysis of FWHM for D- and G- band versus crystallite size; (a)-(b) FWHM of D-band vs. crystallite size (La,Lc), (c)-(d) FWHM of G-band vs. crystallite size (La, Lc).
Table 2.4 Summary of Crystallite Size Measurements of Thermally Treated Carbon Black Series

<table>
<thead>
<tr>
<th>Carbon</th>
<th>La Raman</th>
<th>RSD (%)</th>
<th>La XRD</th>
<th>RSD (%)</th>
<th>Lc</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB1</td>
<td>18.4</td>
<td>1.4</td>
<td>18.6</td>
<td>1.7</td>
<td>15.3</td>
<td>0.8</td>
</tr>
<tr>
<td>CB2</td>
<td>20.7</td>
<td>3.5</td>
<td>21.6</td>
<td>0.5</td>
<td>20.7</td>
<td>0.8</td>
</tr>
<tr>
<td>CB3</td>
<td>22.0</td>
<td>4.1</td>
<td>23.3</td>
<td>1.3</td>
<td>25.9</td>
<td>0.8</td>
</tr>
<tr>
<td>CB4</td>
<td>28.1</td>
<td>1.2</td>
<td>25.5</td>
<td></td>
<td>29.6</td>
<td></td>
</tr>
<tr>
<td>CB5</td>
<td>31.4</td>
<td>0.7</td>
<td>30.7</td>
<td>1.2</td>
<td>32.2</td>
<td>0.4</td>
</tr>
<tr>
<td>CB6</td>
<td>42.4</td>
<td>5.0</td>
<td>43.8</td>
<td>0.8</td>
<td>42.7</td>
<td>1.8</td>
</tr>
</tbody>
</table>

A comment must be made regarding the excitation energy of the laser used for Raman analysis. The relationship between band position and excitation laser energy has been investigated by several researchers\(^ {26-28} \). A strong dependence on band position as a function of excitation wavelength was indicated by each of the researchers. The penetration depth of the laser below the sample surface may alter the observed spectrum. The relationship between excitation wavelength and penetration depth is critical to understand particularly when using confocal Raman micro-spectrometers. The investigation into the impact of excitation wavelength on crystallite size measurements is beyond the scope of the work described here.

Final comparisons of the crystallite size measurements versus relative reactor temperature are provided in Figure 2.10. For both Lc and La (by Raman), the crystallite size of the heat treated carbons increases in a linear fashion. The crystallite size of the untreated carbon was not included in the plot since the sample did not experience a modification in processing. The linear regression of the crystallite size versus relative temperature is statistically significant. The
correlation coefficient shown in Figure 2.10 is 0.967 and 0.985 for \( L_a \) and \( L_c \) measured values respectively.

**Figure 2.11** Regression analysis of crystallite size versus relative reaction temperature a) crystallite diameter from Raman measurements, b) crystallite stacking height from x-ray diffraction measurements

2.3.5 *Transmission Electron Microscopy of Thermally Treated Carbons*

The structure of CB1 and CB6 were inspected by Transmission Electron Microscopy (TEM) as a visual confirmation of the behavior observed in both Raman and x-ray diffraction analyses. TEM images provide the ability to see the aggregate structure of the carbon samples along with details of the primary particle structure. The TEM image of CB1 and CB6 is shown in Figure 2.11. The aggregate structure of both carbons is similar in terms of primary particle size and degree of branching. The structure of the aggregate does not appear to be impacted dramatically during the heat treatment process. The primary particles for CB1 have a mainly
spheroidal shape with noticeable curvature along the edges of the primary particles. The CB6 sample shows changes to the shape of the primary particle. At 30000x magnification, the primary particles appear to have less curvature at the edges. The primary particles appear to have lost some of the diffuse appearance in CB6. A higher magnification image shows why the primary particles have a shift in appearance upon heat treatment. A TEM image of the carbons at 120000x is shown in Figure 2.12.

Figure 2.12 TEM image of carbon black samples at 30000x magnification, a) CB1 untreated carbon black, b) CB6 highest treatment carbon black

A clearer view of the changes to the primary particles is evident at 120000x magnification. The necking between primary particles has a more angular appearance in CB6 versus primary particles from CB1. The organization of layers on the outer portions of the primary particles is visible in CB6 as well. Clearly, heat treatment of the carbon black has modified the within
primary particle structure. The aggregate structure appears to be mainly undisturbed from heat treatment. Final inspection at 300000x magnification (Figure 2.13) provides a view of the crystallite layers in the heat treated carbon black sample. The graphitic layer build-up is clearly evident at 300000x magnification. The angular edges of the primary particles in CB6 are more clearly observed at the higher magnifications. The crystallite thickness appears to be approximately 5 nm which is in good agreement with x-ray measurements. The layers in CB1 appear shorter in length and more randomly organized which agrees with the observations from Raman and x-ray diffraction.

Figure 2.13 TEM image of carbon black samples at 120000x magnification, a) CB1 untreated carbon black, b) CB6 highest treatment carbon black
2.4 Conclusion

The use of x-ray diffraction and Raman spectroscopy to characterize the crystallite size of thermally treated carbon black was shown to be effective. The graphitic content of the carbon black was shown to increase as the treatment temperature increased. The use of peak area instead of intensity for $L_a$ values measured by Raman spectroscopy versus x-ray diffraction was shown to be within good agreement with the empirical relationship from Tuinstra and Koenig$^{12}$. Inspection of electron microscope images for CB1 and CB6 support the observations from the x-ray and Raman analyses. The changes to the carbon black particles with respect to thermal treatment will be used in the evaluation electrochemical stability at potentials at or above 5 V.


Chapter 3  The Carbon Electrode

3.1 Introduction

Carbon black electrodes were subjected to cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements to study the effects of heat treatment on the carbon black used for electrodes. Cyclic voltammetry provides information on the electrochemical processes that happen when the carbon electrode is subjected to potentials above 5 V versus a lithium reference electrode. The degradation of the electrolyte at high voltages is hypothesized to increase the resistances within the carbon electrode cell. Two causes are hypothesized for the degradation as it relates to carbon black. First, oxygen containing functional groups on the surface of carbon black can participate in side reactions with the solvents and salts that make up the electrolyte\(^1\)-\(^2\). The formation of electrode-electrolyte interface (EEI) layers may hinder diffusion to, or from, the electrode surface. In the case of a graphite anode, a layer forms due to the reduction of the electrolyte and solvent molecules at the electrode surface\(^3\)-\(^5\). Growth of the layer upon extensive charge-discharge cycling of the battery will result in reduced capacity over time. The oxidation of the electrolyte is thought to contribute to the formation of the cathode electrolyte (CEI) interface layer\(^6\)-\(^7\). The impact of conductive carbon additives on CEI formation is not as well understood as the SEI at the graphite anode. The second hypothesis for degradation in lithium-ion cells is related to electrolyte starvation. High surface area conductive additives have higher absorption behavior than typical active materials in the cathode. Reduced ion diffusion would result in a cell that is starved of electrolyte. The use of EIS and CV provides a view into the stability of the carbon electrode at potentials above 5 V. The impact of heat treated carbon blacks on the CEI layer and degradation of the electrolyte is of primary interest.
3.1.1 Cyclic Voltammetry Review

Cyclic voltammetry is a linear potential sweep method used often for studying the electrochemical reactions. The current is measured at an electrode as the potential is increased linearly with time in an anodic or positive direction between two potentials. At the upper limit, the scan direction is reversed, and the current is measured as the potential is swept in the cathodic or negative direction. The general waveform for CV experiments is given in Figure 3.1. The electrode is driven to more positive potentials during the forward scan, so that oxidation of species will occur at the electrode surface. During the reverse scan, the potential of the electrode is driven towards less positive potentials, such that the oxidized species at the electrode surface are reduced. During the anodic scan measured currents are negative, however the convention is to plot the anodic currents as positive values. Cathodic currents are plotted as negative values.

Figure 3.1 Waveform for cyclic voltammetry experiment; Forward scan is anodic and reverse scan is cathodic
An example of a CV scan is shown in Figure 3.2. The peak potentials, and the corresponding peak currents, for the anodic and cathodic scans are important values to determine.

![CV Scan Diagram](image)

**Figure 3.2** Example cyclic voltammetry scan of 8mM ferrocene in lithium ion battery electrolyte solution with the anodic and cathodic peaks ($E_{p_a}$, $E_{p_c}$) and currents ($i_{p_a}$, $i_{p_c}$) labelled

The reversibility of an electrochemical reaction is observed with the mirror image shape of the CV scan for a faradaic process. For non-faradaic processes, the scan should appear more rectangular.

The area of the electrode, diffusion coefficients of the oxidant and reductant, and the concentration of species in the cell are all examples of values that can be determined through CV
experimentation. A more detailed explanation of cyclic voltammetry is provided in Bard and Faulkner⁸.

3.1.2 Electrochemical Impedance Spectroscopy Review

Electrochemical Impedance Spectroscopy involves measuring the current response from a coin cell, in this case, while a small AC potential is applied to the cell. The potential is not large enough to induce polarization in the cell. The purpose of the AC potential is to perturb the cell without altering the state of charge of the battery cell. Visualization of the EIS results is commonly done using a Nyquist or Bode plot. For the Nyquist plot, the imaginary component of the impedance, $Z_{\text{img}}$, is plotted versus the real component of the impedance, $Z_{\text{real}}$. For carbon electrodes, the Nyquist plot has a semi-circular portion and an increasing linear region present. A Nyquist plot for a model sample is shown in Figure 3.3.

![Figure 3.3 Example EIS of a model sample](image)

Figure 3.3 Example EIS of a model sample
One significant issue with the Nyquist plot is the lack of information regarding the relationship between the real and imaginary components of the impedance and the frequency. An alternative plot is needed to provide the link between the impedance response and frequency. The Bode plot provides the visual presentation of the impedance behavior of a cell with respect to the frequency. For the Bode plot, the absolute impedance, $|Z|$ (Equation 3.2), is plotted on the $y$-axis versus the frequency in Hz. The typical response appears as a sigmoidal curve increasing from right to left. A general example of the Bode plot is shown in Figure 3.16.

$$\omega_{\text{max}} = \frac{1}{C_{dl}R_{ct}}$$  \hspace{1cm} (3.1)

**Figure 3.4** Example of Bode plot where total impedance is plotted vs. frequency in Hz
|Z| = \sqrt{Z_{\text{real}}^2 + Z_{\text{imaginary}}^2} \quad (3.2)

Interpretation of the impedance results for a battery cell is done by building equivalent circuit models. A theoretical circuit design can be mathematically modelled to simulate the impedance measured for the actual battery. The resistance and capacitance values modelled in the equivalent circuit can then be used to explain the behavior of the battery cell. Caution must be exercised while developing an equivalent circuit. The circuit is not mutually exclusive to the battery itself. In other words, many equivalent circuits can be designed that appropriately describe the impedance response for a battery. The onus is on the researcher to provide a reasonable explanation for the components used in the circuit. The equivalent circuit modelling is similar to regression modelling in that the goodness-of-fit of the model always improves as additional components are added to the model. Every researcher must avoid creating a circuit that provides a good fit to the impedance response without justification for the components in the model.

3.2 Experimental

3.2.1 Carbon black paste

A paste of 8% carbon black by weight was made for fabrication of the carbon electrodes. The paste consisted of 8% carbon black, 6% polyvinylidene fluoride (PVDF), and N-methyl pyrrolidone (NMP) as the balance. A planetary centrifugal mixer (Thinky Mixer ARE-310) was used to prepare the carbon black pastes. The mixing program consisted of 4 alternating cycles of
mixing and rest to avoid excess heat generation during paste processing. Heat is generated during the paste process due to the high viscosity of the material.

3.2.2 Electrode Film Coating

A film coater apparatus was used to apply a uniform layer of carbon paste to the surface of an aluminum foil current collector. The gap set on the draw down blade was 0.10 mils. The coated foil was pre-dried on an aluminum plate that was preheated to 85°C. The pre-drying step was conducted in a fume hood to remove most of the NMP solvent prior to final drying. The film was dried a minimum of 4 hours at 85°C. The dried coating consisted of 80% carbon black and 20% PVDF by weight.

3.2.3 Coin Cell Assembly

Carbon black electrodes with a diameter of 15 mm were cut from the casted foil using a die press. The carbon electrode disks were placed in a vacuum oven at 100°C for a minimum of 16 h prior to use in a coin cell. After vacuum drying, the electrodes were weighed and transferred to an argon purged glove box for assembly in coin cells. The 2032 type coin cell was used for the carbon electrode measurements. The oxygen and water levels in the glove box are maintained below 1 ppm to minimize the impact on the components of the cell (i.e. electrolyte, lithium foil, carbon electrode, etc.). The general coin cell construction is shown in Figure 3.5. A 16 mm disk of lithium foil is placed in the bottom of the coin cell casing. A in-house fabricated plunger was used to press the lithium foil into the coin cell assembly to ensure good contact with the bottom of the cell. The separator for the cell is a 17 mm Whatman glass fiber disk. The electrolyte consisted of 1 M LiPF₆ in a 1:1:1 mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). The volume of electrolyte used in each carbon
The electrode cell was 100 µL. The carbon electrode was placed on top of the separator with the carbon surface facing towards the lithium foil. A stainless steel spacer and wavy spring were placed on top of the bare aluminum side of the carbon electrode. Finally, the top of the coin cell was put in place. The coin cell was sealed using a Hohsen Corp. automatic coin cell crimper.

![Diagram of coin cell with carbon electrode](image)

**Figure 3.5** 2032 coin cell with carbon electrode

Cells were allowed to sit undisturbed for 24 hours at room temperature to allow the electrolyte to properly wet the surface of the electrodes and separator.

### 3.2.4 Cyclic Voltammetry

Cyclic voltammetry experiments were conducted using a Parstat 2273 potentiostat from Princeton Applied Research. The vertex limits were set at 5.1V and 1.5V for most of the voltammetry measurements. The default scan rate for the CV measurements was set to \( \square = \)

10mV/s. Three scans were collected for the typical carbon electrode coin cell. Specific measurements were also made using varying scan rates and number of cycles collected.

### 3.2.5 EIS Experimental

Electrochemical Impedance Spectroscopy measurements were completed on the 2032 coin cells using the Parstat 2273 instrument. The EIS measurements provide the ability to evaluate the resistances, capacitances, and diffusion characteristics of the coin cell after polarization. Carbon electrode cells were measured in the frequency range from 100 kHz to 100 mHz with an AC potential difference of 10 mV rms. Ten data points per decade of frequency were collected for each cell. Equivalent circuit modelling was performed using the ZfitGUI (varigin).9

### 3.2.6 Surface Area and Structure Measurements of Carbon Black

Table 3.1 provides common characteristic measurements for carbon black. Two surface area measurements are reported for the carbon black samples. Total surface area is measured using the Brunauer-Emmet-Teller model10 more widely known as BET surface area. Statistical Thickness Surface Area (STSA) is a measure of the external surface area of a solid. A single gas adsorption measurement provides the results for both measurements as long as the appropriate relative pressure range is used. Unfortunately, STSA measurements were not collected for all of the heat treated samples. The difference between total and external surface area appears to decrease as samples are thermally treated. More results are needed to confirm the relationship between STSA and heat treatment, but a brief view seems to support loss of some level of pore structure with increasing temperature. Oil Adsorption Number (OAN) is a standard measurement used to characterize the structure of carbon black. The OAN method involves
measuring the torque of a mixture as oil is added drop wise to a chamber filled with carbon black. As the volume of oil reaches a point of full surface coverage, the torque rises very quickly. The reported value is the volume at 70% maximum torque. The units of the measurement are milliliters of oil per hundred grams of carbon black powder.

<table>
<thead>
<tr>
<th>Table 3.1 Surface Area and Structure Measurements of Carbon Black</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET (m²/g)</td>
</tr>
<tr>
<td>CB1</td>
</tr>
<tr>
<td>CB3</td>
</tr>
<tr>
<td>CB4</td>
</tr>
<tr>
<td>CB5</td>
</tr>
<tr>
<td>CB6</td>
</tr>
</tbody>
</table>

The structure of the carbon black does not appear to be impacted by heat treatment, which is consistent with the observations from the TEM images reported in chapter 2.

3.3 Results and Discussion

3.3.1 Cyclic Voltammetry of Carbon Electrodes

Cyclic voltammetry was used as a qualitative tool in the investigation of the carbon electrode behavior. The current response of the carbon electrode was collected as the potential was linearly increased from 1.5 V to 5.1 V. For carbon electrodes, the shape of the CV curve is expected to be nearly featureless as no electrochemically active material is present in the cathode. First, coin cells with carbon electrodes were measured at room temperature. Coin cells
from three carbon types were measured at elevated temperature to evaluate how elevated temperature effected the voltammetry response of the carbon electrode.

A plot of the current vs. potential for carbon CB1 is shown in Figure 3.6. The value for current was normalized for the mass of carbon and binder present in the electrode. Three scan cycles were collected at a rate, \( v = 10 \text{ mV/s} \). A subtle anodic peak at 3.92 V vs. \( \text{Li/Li}^+ \) can be seen on the first cycle with a corresponding cathodic peak at 3.72 V vs. \( \text{Li/Li}^+ \). The anodic and cathodic peaks shift slightly on scans 2 and 3, but both are still present. The peaks in the CB1 scan have been assigned to surface reactions occurring between the electrolyte and the surface functional groups on the carbon black similar in nature to the observations of Qi et al\(^{11}\). Previous work on graphitized carbon black has shown a high degree of surface reaction for untreated carbon black in LiNi\(_{0.43}\)Mn\(_{1.5}\)Cr\(_{0.07}\)O\(_4\) compositie cathodes\(^{12}\). Reaction between the surface functional groups on the untreated carbon black appears valid in the absence of electrochemically active material. The CV scans for heat treated carbon black electrodes look similar to CB1 with a few additional features.

In Figure 3.7, the CV scans of each carbon electrode are shown. The first obvious feature is the peak for CB1 at 3.92 V has shifted in the heat treated carbons to approximately 4.1 V. Some variability in the position and shape can be seen in the peak at 4.1 V. At the highest level of treatment, CB6 shows the smallest peak current at 4.1V, but clearly some level reaction between the carbon surface and the electrolyte is occurring. Research by La Mantia and Huggin\(^{13}\) theorized that a plateau in charge-discharge cycling at 4.1 V was due to water adsorbed on the surface of the carbon. In their work, heating the carbon electrodes above 150°C in an argon filled glovebox removed the plateau at 4.1 V completely. A second plateau at 4.6 V was
present for the Super P study which was identified by La Mantia and Huggin as the SEI layer formation. The findings by La Mantia and Huggin appear to directly contrast the identification made by Qi et al. The oxidation potential for water (vs. Li/Li⁺) is 4.27 V, according to the standard electrode potential table. The peak at 4.1 V in the carbon electrodes in this research could possibly be the result of oxidation of water. Lin et al. conducted similar studies on a variety of conductive carbon additives including Super P and Acetylene Black from TIMCAL Ltd, Switzerland. Cyclic voltammetry scans of carbon electrodes in 1M LiPF6 dissolved in dimethyl carbonate (DMC) showed subtle features similar to those observed in the heat treated carbons in Figure 3.3. Lin et al. indicate the decomposition of electrolyte occurs at 3.75 V (vs. Li/Li⁺) which is in reasonable agreement with the observations by Qi et al. The peak at 4.25 V appears to show up in the second cycle for Super P. The focus of features above 3.75 V (vs. Li/Li⁺) was on the intercalation of PF6⁻ in the variety of carbons, so the subtle features were not discussed. Work done by Zheng et al. also showed the presence of subtle features around 4.25 V for conductive carbons like Super P, Ketjen black, and Acetylene Black. As in the previously discussed studies, the work was mainly focused on anion intercalation near 5 V instead of the subtle features in the scan. Several research efforts show evidence that carbon electrodes exhibit a peak that is near the potential for the oxidation of water. The pronounced peak is not observed in the 2nd cycle or beyond for the heat treated carbons in this work, and only subtle peaks were observed for other conductive carbons. Lin et al. proposed an alternative hypothesis to the behavior observed in terms of heated electrodes. The possibility that heating the electrodes may have caused the binder to migrate, providing better coverage of the porous electrode surface, was proposed as an alternative to removal of water. With the porous nature of the carbon structure, water adsorption should occur well into the pore structure. It is reasonable to assume that water
would be difficult to remove from pores of carbon black. Typical degasing conditions for nitrogen surface area measurements provide some support for the difficulty in removing water and other volatile materials from carbon black. Samples are heated to temperatures of 300°C under an inert atmosphere for periods > 1h depending on the nature of the material and the purpose of the measurement (e.g. BET surface area, pore distribution, etc.). Everett and Ward\textsuperscript{16} studied the water adsorption of graphitized Vulcan 3 carbon black and found that the uptake of water was greatly reduced after heat treatment above 1000°C. The adsorption-desorption curves for water show hysteresis which indicates that water loss is not complete. Further observations from Everett and Ward show an ageing effect on graphitized carbon black materials where water is retained upon re-exposure up to full saturation. Further work would be needed to clearly identify water as the source of the oxidation peak at 4.25 V (\textit{vs}. Li/Li\textsuperscript{+}) for the heat treated carbon black samples examined in this study. Future work might include equilibration of carbon electrodes in various relative humidity environments to allow for moisture uptake prior to electrochemical testing.
Figure 3.6 Cyclic Voltammetry of CB1 carbon electrode in 1M LiPF$_6$/EC:DMC:DEC electrolyte with lithium foil used as reference and counter electrode
Figure 3.7 Cyclic Voltammetry scans of carbon electrodes CB1 – CB6 in 1M LiPF$_6$/EC:DMC:DEC electrolyte with lithium foil used as reference and counter electrode
3.3.2 PF₆⁻ Intercalation in Electrodes of Heat Treated Carbon Black

Anion intercalation is observed in the CV scans given in Figure 3.8, in particular for samples that have experienced higher relative treatment temperatures. The work by Qi et al., Zheng et al., and Lin et al., show intercalation of anions in electrodes made with graphitized carbon black.

![CV scan of CB3, CB5, and CB6; PF₆⁻ intercalation in graphitized carbon black](image)

**Figure 3.8** CV scan of CB3, CB5, and CB6; PF₆⁻ intercalation in graphitized carbon black

The intercalation anodic peak corresponding to intercalation of PF₆⁻ is observed between 4.8 and 4.95 V (vs. Li/Li⁺) depending on the carbon electrode and the scan rate. Cathodic peaks for the de-intercalation of PF₆⁻ are observed in the CV scans as well. One peak at 4.12 V (vs. Li/Li⁺)
Li/Li\(^+\)) is evident in the CB5 scan. The CB6 electrode shows two cathodic peaks at 4.55 V and 4.11 V (vs. Li/Li\(^+\)) respectively. The anodic and cathodic currents for CB6 electrode is greater than that observed for CB5 indicating the amount of PF6- entering and leaving the carbon structure is higher for the more graphitic carbon. The CB3 electrode shows no anion intercalation in either the anodic or cathodic scans. Although not shown in Figure 3.4, CB 1 does not have peaks consistent with anion intercalation or de-intercalation either. A plot of current density normalized to the surface area of the carbon black (Figure 3.9) provides a clearer view of the anodic and cathodic peaks related to anion intercalation.

![Figure 3.9 CV scan of CB3-CB6 electrodes normalized to surface area of carbon black](image)

Normalization enhances a very small anodic peak in the CB3 electrode at 4.95 V consistent with the anion intercalation. When the current was normalized to the mass of carbon
black and binder, the anodic peak was difficult to see. The corresponding cathodic peaks are absent for CB3 electrodes. CB6 electrodes are the best candidates to look further into anion intercalation.

Figure 3.10 CV scan of CB6 at various scan rates: $v = 10 \text{ mV/s}, 1 \text{ mV/s}, 0.15 \text{ mV/s}, 0.10 \text{ mV/s}$
The plot in Figure 3.10 shows the CB6 electrode at different scan rates. The intent was to calculate the diffusion coefficient associated with PF$_6^-$ ions. The calculation proved to be challenging due to the shift in the intercalation peak by scan rate. Anodic current values were determined from a baseline equal to zero current. The lowest scan rates (100 µV/s, 150 µV/s) gave anodic peaks, $E_{p_a}$ at 4.699 and 4.692 V respectively. As the scan rate increased, the position of the anodic peak for intercalation moved to higher potential. Table 3.2 summarizes the $E_{p_a}$ values by scan rate. A note of caution must be given on the $E_{p_a}$ values for both the 50 and 100 mV/s rate experiments. In both cases, the anodic peak was not well distinguished. Based on the change in peak position with scan rate, the results for 50 and 100 mV/s scans require replication to provide a more accurate estimate of the anodic peak position.

**Table 3.2 Diffusion Study of PF6- Intercalation into Graphitized Carbon Electrode**

<table>
<thead>
<tr>
<th>v (mV/s)</th>
<th>$E_{p_a}$ (V)</th>
<th>$i_p$ (A)</th>
<th>$v^{1/2}$ (V$^{1/2}$/s$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4.70</td>
<td>1.58E-05</td>
<td>0.010</td>
</tr>
<tr>
<td>0.15</td>
<td>4.69</td>
<td>1.37E-05</td>
<td>0.012</td>
</tr>
<tr>
<td>1</td>
<td>4.73</td>
<td>6.64E-05</td>
<td>0.032</td>
</tr>
<tr>
<td>10</td>
<td>4.85</td>
<td>4.77E-04</td>
<td>0.100</td>
</tr>
<tr>
<td>50</td>
<td>4.95</td>
<td>1.90E-03</td>
<td>0.224</td>
</tr>
<tr>
<td>100</td>
<td>4.95</td>
<td>2.14E-03</td>
<td>0.316</td>
</tr>
</tbody>
</table>

An attempt was made to calculate the diffusion coefficient of LiPF6 in the carbonate solvent mixture used in the coin cell. Figure 3.11 shows a plot of anodic peak current versus the square root of the scan rate. The plot uses the relationship from the Randles-Sevcik equation.
(3.3) where the peak current is directly proportional to the square root of the scan rate. The slope of the linear regression can be used to calculate the diffusion coefficient. The equation is

\[ i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \]  \hspace{1cm} (3.3)

where \( n \) is the number of electrons transferred, \( A \) is the area of the electrode (cm\(^2\)), \( D \) is the diffusion coefficient (cm\(^2\)/s), \( C \) is the concentration of the species (moles/cm\(^3\)), and \( v \) is the scan rate (V/s).

![Figure 3.11 Plot of anodic current vs. \( v^{1/2} \) for LiPF6 diffusion in carbon electrode coin cell](image)

The plot of current vs. \( v^{1/2} \) shows a statistically significant linear relationship. The value of \( R^2 \) indicates that the fit accounts for over 96% of the variability in the measured values. The regression was deemed to be a high enough quality to use for the estimation of the diffusion
coefficient. The slope of the regression line now represents the expression shown in Equation 3.4

\[
slope = 2.69 \times 10^5 n^{3/2} AD^{1/2} C
\]  

(3.4)

The area of the electrode was not strictly known, so the geometric area was used as a first approximation to estimate the diffusion coefficient of PF$_6^-$.

In order to find the diffusion coefficient, equation 3.4 was rearranged to solve for D as shown in equation 3.5.

\[
D = \frac{(slope)^2}{\frac{3}{4} (2.69 \times 10^5 n^{3/2} AC)^2}
\]  

(3.5)

The geometric area of a 15 mm disc is equal to approximately 1.77 cm$^2$. Assuming $n = 1$, the diffusion coefficient, D, was estimated as 2.58x10$^{-10}$ cm$^2$/s. For the EC:DMC:DEC solvent system, a reference for diffusion of PF$_6^-$ was not found. However, diffusion of PF$_6^-$ was estimated in binary mixtures of EC and DEC$^{17}$, along with several other combinations. The diffusion coefficient in single solvent systems were also determined in the work by Hayamizu$^{17}$. The values of D for PF$_6^-$ at 293 K ranged from 1.76 x10$^{-6}$ cm$^2$/s to 2.15x10$^{-6}$ cm$^2$/s, which is in reasonable agreement with studies performed using PC:EC:DMC$^{18}$ or EC:DEC$^{19}$ solvent mixtures. In the study of the heat treated carbon electrodes, the diffusion of PF$_6^-$ was found to be 4 orders of magnitude lower than the coefficients found in the literature. Low anodic current values could be the result of either poor reversibility of the intercalation process or high solvent uptake by the carbon black. Poor reversibility or de-intercalation would be the result of structure changes in the carbon black layers effectively trapping the PF$_6^-$ anion in the carbon particle.

Read studied the intercalation of PF$_6^-$ in graphite structures using in situ XRD$^{20}$. The graphite
layer spacing was shown to increase in order to accommodate the PF$_6^-$ anion. Solvent molecules were also intercalated along with the anion. Syzdek et al.\textsuperscript{21} used ex situ Raman analysis to show similar changes in structure of acetylene blacks from intercalation of PF$_6^-$. Syzdek \textit{et al.} claim the structure change in the ordered regions of carbon black particles could result in entrapment of PF$_6^-$ upon intercalation.

A 50 cycle scan measurement was conducted on the CB6 electrode to observe the changes to the electrode performance during a moderate number of CV scans.

Figure 3.12 CV scan of CB6 coin cell cycled 50 times between 2.5V and 5.1V vs. Li/Li+

Figure 3.12 shows a full scale view of the 50 cycles of the CB6 electrode. Scans colored purple represent the first 5 cycles. Figure 3.13 is an expanded view of the region between 4.5 V and 5.1 V for the 50 cycle measurement. The first observation is the current measured at 5.1 V increases
on each of the first 5 cycles. The current at cycle 5 is double that observed for cycle 1. The anodic peak assigned to PF$_6^-$ intercalation appears to be mainly absent for the first 5 cycles, which is in contradiction to the 3 cycle experiments collected previously. After cycle 5, the current at 5.1 V steadily decreases. The current at 5.1 V approaches a limiting value as the cycle number increases. Figure 3.14 shows the peak current as a function of measurement time. At cycle 6, the first indication of anion intercalation is seen in the CV scan of the cell. A second anodic peak begins to grow in at approximately 4.85 V. As the cycle numbers approach 50, two distinct peaks are present in the anodic portion of the curves (Figure 3.15). Both peaks (4.85 V and 4.98 V) have been identified as arising from intercalation of PF$_6^-$ and associated solvents in the literature$^{11,14-15}$. While both anodic peaks may arise from anion intercalation, it is obvious that the mechanism of intercalation is different. Further study is needed to understand the origin of the two anodic peaks. The discrepancy in the diffusion coefficient for PF6- remains unresolved at this point. Investigation of the carbon electrode using Electrochemical Impedance Spectroscopy (EIS) may provide a clearer picture of the diffusion limitations.
**Figure 3.13** Expanded view of CB6 coin cell cycled 50 times from 2.5V to 5.1V

**Figure 3.14** Plot of current vs Time for CB6 cell cycled between 5.1V and 2.5V vs. Li/Li+ for 50 cycles
3.3.3 Carbon Electrode Cyclic Voltammetry at Elevated Temperature

A few comments are needed regarding the voltammetry evaluation of carbon electrodes at elevated temperature. Three carbons were selected to be evaluated at 74°C (CB1, CB2, CB6). The carbons represent no heat treatment, moderate, and high levels of heat treatment respectively. Cyclic voltammetry was not expected to provide additional information as to the room temperature experiments. The purpose of cycling carbon electrodes at elevated temperature was to understand what happens to resistances and capacitances by EIS when a coin cell is subjected to elevated temperature. The CV scans were collected as a matter of due diligence. Figures 3.16, 3.17, and 3.18 show the CV scans for the selected carbons at 74°C and 21°C. The current density is larger for the elevated temperature experiments as expected. The diffusion of ions in the coin cell is proportional to the temperature, so migration to the electrode surface happens at a faster rate for experiments at 74°C. The current observed at 5.1 V decreases
in each successive cycle as have been observed with CV scans at 21°C. Finally, the CB6 scans show a much more definitive PF6- intercalation peak at 74°C versus 21°C. Further comments on the coin cells subjected to elevated temperature is reserved for the EIS discussion.

Figure 3.16 CV measurement of CB1 at 21°C (blue) and 74°C (red); Potential range from 1.5V to 5.1V in 1M LiPF₆/EC:DMC:DEC electrolyte
Figure 3.17 CV measurement of CB2 at 21°C (blue) and 74°C (red); Potential range from 1.5V to 5.1V in 1M LiPF$_6$/EC:DMC:DEC electrolyte

Figure 3.18 CV measurement of CB6 at 21°C (blue) and 74°C (red); Potential range from 1.5V to 5.1V in 1M LiPF$_6$/EC:DMC:DEC electrolyte
3.3.4 Electrochemical Impedance Spectroscopy of Carbon Electrodes

The impedance behavior of the carbon electrode is similar to that of a simple Randle circuit\textsuperscript{22}. A Randle circuit consists of a resistor in series with a parallel combination of a capacitor and a resistor. The Randle circuit is shown in Figure 3.19. The solution resistance, $R_e$, can be estimated by finding the point of intersection with the real axis at the left hand portion of the Nyquist plot. The charge transfer resistance, $R_{ct}$, can be estimated using the right portion of the semicircle. The double layer capacitance, $C_{dl}$, can be estimated from the maximum height of the semicircle. The maximum point of the semicircle along the imaginary axis, $\omega_{\text{max}}$, is related to $C_{dl}$ by equation (3.1).

Before proceeding, the impedance for common circuit elements needs to be defined. The relationships that describe the impedance for each of the elements listed here can be readily found in the literature\textsuperscript{8, 23-25}. The following series of equations will define the impedance for each element used in the evaluation of the heat treated carbon black electrodes. First, the impedance of a resistor is quite simply,

$$Z_{\text{resistor}} = R$$  \hspace{1cm} (3.6)

The impedance for a capacitor is

$$Z_{\text{capacitor}} = \frac{1}{j\omega C}$$  \hspace{1cm} (3.7)
where \( j \) is the imaginary number equivalent to \((-1)^{1/2}\), \( \omega \) is the angular frequency in rad/s, and \( C \) is the capacitance in farads (F). The impedance of a Constant Phase Element (CPE) is defined as

\[
Z_{CPE} = \frac{1}{(Q^0 j \omega)^n}
\]  

(3.8)

where \( Q^0 \) is equal to the admittance \((1/|Z|)\) at \( \omega = 1 \) rad/s, \( \omega \) and \( j \) are as previously defined, and \( n \) is a dimensionless exponent related to the degree of depression in the semicircle portion of the Nyquist plot. When \( n=1 \), Equation 3.8 becomes the impedance for a capacitor (3.7). A CPE has a phase angle that is less than 90° by a factor of \( n \). The Warburg element is a specific type of CPE that has a phase angle equal to 45°. Warburg elements are used to account for diffusion in the impedance response. The Warburg element is defined as

\[
Z_W = \frac{\sigma}{\sqrt{\omega}} - \frac{j \sigma}{\sqrt{\omega}}
\]  

(3.9)

where \( j \) and \( \omega \) are as previously defined, and \( \sigma \) is the Warburg coefficient. The equation for \( s \) is

\[
\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left( \frac{1}{D_O^{1/2} C_O^b} + \frac{1}{D_R^{1/2} C_R^b} \right)
\]  

(3.10)

where \( R \) is the gas constant, \( T \) is the temperature in Kelvin, \( n \) is the number of electrons, \( F \) is Faraday’s constant, \( D \) is the diffusion coefficient with \( O \) and \( R \) representing oxidized or reduced forms of the species, and \( C \) is the concentration in the bulk solution.

An examination of the Bode and Nyquist plots for a selection of carbon black samples provides some insight into the differences in the samples. Figure 3.20 shows the Bode plot for
the carbon electrode, and the Nyquist plot is given in Figure 3.21. In Figure 3.21, the plot was zoomed in to see the semi-circle portion of the response from the carbon electrodes. In both the Nyquist and Bode plots of CB1, CB2, and CB6 replicate coin cells, it is clear that coin to coin variability is quite different between the carbon types. The impedance responses of CB6 electrodes show a high level of consistency. The variability observed for both CB1 and CB2 electrodes is very high by comparison. The solution resistance, $R_e$, is approximately the same for the carbon types, but the charge transfer resistance, $R_{ct}$, is very different based on the right hand portion of the semicircle of the Nyquist plot. In the Bode plot, the two plateaus are used to estimate the value of the resistances, $R_e$ and $R_{ct}$. The second plateau, between 1kHz and 1 Hz, shows a large difference in total impedance between carbon electrodes. The first conclusion drawn from EIS results is that CB6 electrodes are more reproducible than either CB1 or CB2. The remaining carbon types will be evaluated in more detail below.

A Randle circuit was used first to fit the impedance plots from the heat treated carbon samples. The Randle circuit model was fit to the measured impedance response for each of the carbon electrode coin cells. The Randle circuit as shown in Figure 3.19 has poor agreement with measured response for the semicircle portion of the Nyquist plot for all of the carbons. The tail portion of the Nyquist plot is not fit using only a resistor in series with a capacitor and resistor in parallel. The depressed semicircle portion of the measured impedance indicates that the carbon electrode does not behave as a true capacitor. A constant phase element is used as a replacement for the capacitor in the model. In addition, another element is needed to model the increasing tail, or low frequency, portion of the Nyquist plot. The behavior in the low frequency range is
related to diffusional behavior of the electrode, which is modeled using either a transmission line element or a Warburg element.

![Diagram of a Randle circuit](image)

**Figure 3.19:** General diagram for a Randle circuit
In order to better describe the behavior of the carbon electrode, a CPE was used in place of the capacitor, and a Warburg element was added to the model. The modeled fit using a CPE and Warburg element in the circuit does not have an acceptable fit to the measured response as can be seen in Figure 3.23. The capacitive portion of the impedance spectrum is not well described with a traditional Warburg element. The indication is that infinite diffusion is not present, but the diffusion is finite or bounded in some way. Bounded diffusion is common in porous electrodes and in particular for electrodes that have some coating that limits the access species have to the electrode surface\textsuperscript{24, 26-27}. The work by Kang and Kwon claim three processes contribute the impedance for a carbon electrode. The process occurring between the bulk
electrolyte and the diffuse layer is accounted for using the solution resistance, the parallel arrangement of a CPE and resistor along with the Warburg element to account for diffusion. The other processes occur in the Inner Helmholtz Plane and at the electrode surface.

![Figure 3.21 Nyquist plot of CB1 (red), CB2 (blue), and CB6 (green) carbon electrode coin cells](image)

Figure 3.21 Nyquist plot of CB1 (red), CB2 (blue), and CB6 (green) carbon electrode coin cells

Table 3.3 summarizes the equivalent circuit models used for the carbon electrodes using heat treated carbon black. The first two models were shown to be poor in terms of modeling the impedance behavior of the carbon black electrode (Figs 3.22 and 3.23). The third model incorporating the approach by Kang\textsuperscript{24} and Kwon\textsuperscript{27} was applied to the carbon electrodes used in this work. The Warburg element at semi-infinite diffusion was replaced with the short circuited Warburg finite diffusion element due to the improved fit. Replacing the Warburg element with a
finite diffusion Warburg element is common for modeling batteries, when a fixed amount of the active species is expected to be present in the layer near the electrode surface.

The EIS response for CB1 through CB6, excluding CB4, were fit using the ZfitGUI (varigin) application. The application minimizes the $\chi^2$ sum to provide a goodness of fit parameter (Equation 3.14). The three process model was shown to be effective in simulating the measured EIS response for each of the carbon electrodes. The fit statistic, $\chi^2$, was less than 0.1 for all simulations of the coin cells. Figure 3.24 provides example Nyquist and Bode plots for CB1, CB2, and CB6 with the simulated fits included.

![Nyquist plot](image)

**Figure 3.22** Nyquist plot for CB2 coin cell with Randle circuit model fit
**Figure 3.23** Nyquist plot of CB2 coin cell with Randle circuit model fit with CPE and Warburg element added

**Table 3.3** Equivalent Circuit Models with Corresponding Equation for Total Impedance

\[
Z = R_1 + \left( \frac{1}{Z_{CPE1}} + \frac{1}{Z_W} \right)^{-1} \tag{3.11}
\]

\[
Z = R_1 + \left( \frac{1}{Z_{CPE1}} + \frac{1}{Z_{CPE2}} + \frac{1}{Z_W} \right)^{-1} \tag{3.12}
\]

\[
Z = R_1 + \left[ \frac{1}{Z_{CPE1}} + \frac{1}{R_2 + Z_W + \left( \frac{1}{Z_{CPE2}} + \frac{1}{R_3 + C_3} \right)^{-1}} \right]^{-1} \tag{3.13}
\]
The values for each circuit element in the model were determined for each coin cell tested. Table 3.4 summarizes the results of each circuit element calculated from the simulation.

**Table 3.4 Calculated Results from EIS Simulation Fits**

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Coin</th>
<th>R1 (W)</th>
<th>Q1 (S·s⁻¹)</th>
<th>n1</th>
<th>R2 (W)</th>
<th>Y₀ (S)</th>
<th>B</th>
<th>Q2 (S·s⁻¹)</th>
<th>n2</th>
<th>R3 (W)</th>
<th>C1 (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB1</td>
<td>24</td>
<td>6.406</td>
<td>8.62E-06</td>
<td>0.866</td>
<td>44.49</td>
<td>0.04606</td>
<td>0.7369</td>
<td>5.74E-03</td>
<td>0.9323</td>
<td>74.77</td>
<td>3.79E-03</td>
</tr>
<tr>
<td>CB1</td>
<td>25</td>
<td>3.66</td>
<td>1.11E-05</td>
<td>0.8364</td>
<td>62.66</td>
<td>0.05364</td>
<td>0.8587</td>
<td>5.55E-03</td>
<td>0.7946</td>
<td>60.09</td>
<td>2.78E-03</td>
</tr>
<tr>
<td>CB1</td>
<td>28</td>
<td>4.256</td>
<td>1.26E-05</td>
<td>0.8269</td>
<td>51.32</td>
<td>0.06367</td>
<td>0.1995</td>
<td>7.54E-03</td>
<td>0.8592</td>
<td>85.34</td>
<td>2.70E-03</td>
</tr>
<tr>
<td>CB2</td>
<td>50</td>
<td>2.483</td>
<td>1.55E-05</td>
<td>0.796</td>
<td>102</td>
<td>0.03937</td>
<td>0.3034</td>
<td>1.07E-02</td>
<td>0.7826</td>
<td>40.83</td>
<td>1.97E-05</td>
</tr>
<tr>
<td>CB2</td>
<td>51</td>
<td>5.511</td>
<td>1.84E-05</td>
<td>0.7907</td>
<td>71.79</td>
<td>0.06506</td>
<td>0.2769</td>
<td>1.18E-02</td>
<td>0.8215</td>
<td>24.31</td>
<td>4.36E-05</td>
</tr>
<tr>
<td>CB2</td>
<td>52</td>
<td>2.221</td>
<td>1.61E-05</td>
<td>0.8143</td>
<td>53.64</td>
<td>0.0766</td>
<td>0.2869</td>
<td>1.22E-02</td>
<td>0.8439</td>
<td>18.57</td>
<td>5.68E-05</td>
</tr>
<tr>
<td>CB3</td>
<td>15</td>
<td>2.797</td>
<td>9.95E-06</td>
<td>0.8487</td>
<td>55.67</td>
<td>0.03711</td>
<td>0.4022</td>
<td>3.50E-03</td>
<td>0.9423</td>
<td>18.85</td>
<td>4.27E-04</td>
</tr>
<tr>
<td>CB3</td>
<td>16</td>
<td>2.326</td>
<td>1.21E-05</td>
<td>0.8301</td>
<td>57.23</td>
<td>0.05474</td>
<td>0.4511</td>
<td>2.69E-03</td>
<td>0.9516</td>
<td>21.67</td>
<td>9.55E-04</td>
</tr>
<tr>
<td>CB5</td>
<td>18</td>
<td>1.691</td>
<td>1.04E-05</td>
<td>0.8504</td>
<td>50.97</td>
<td>0.05871</td>
<td>0.4987</td>
<td>2.00E-03</td>
<td>0.9298</td>
<td>39.44</td>
<td>9.34E-04</td>
</tr>
<tr>
<td>CB5</td>
<td>19</td>
<td>2.401</td>
<td>9.88E-06</td>
<td>0.8558</td>
<td>53.52</td>
<td>0.02818</td>
<td>0.5096</td>
<td>2.28E-03</td>
<td>0.9504</td>
<td>38.2</td>
<td>8.88E-04</td>
</tr>
<tr>
<td>CB5</td>
<td>20</td>
<td>2.565</td>
<td>1.13E-05</td>
<td>0.8513</td>
<td>45.74</td>
<td>0.04105</td>
<td>0.4814</td>
<td>3.86E-03</td>
<td>0.9473</td>
<td>34.03</td>
<td>1.10E-03</td>
</tr>
<tr>
<td>CB6</td>
<td>21</td>
<td>2.486</td>
<td>9.15E-06</td>
<td>0.8634</td>
<td>53.64</td>
<td>0.0583</td>
<td>0.9</td>
<td>3.63E-03</td>
<td>0.9828</td>
<td>27.92</td>
<td>1.92E-03</td>
</tr>
<tr>
<td>CB6</td>
<td>23</td>
<td>2.55</td>
<td>1.27E-05</td>
<td>0.8262</td>
<td>55.5</td>
<td>0.04549</td>
<td>0.5649</td>
<td>3.05E-03</td>
<td>0.9444</td>
<td>29.41</td>
<td>1.59E-03</td>
</tr>
<tr>
<td>CB6</td>
<td>27</td>
<td>2.218</td>
<td>9.59E-06</td>
<td>0.8582</td>
<td>53.68</td>
<td>0.05135</td>
<td>0.9208</td>
<td>2.70E-03</td>
<td>0.9525</td>
<td>26.37</td>
<td>2.51E-03</td>
</tr>
</tbody>
</table>

The values Y₀ and B are obtained from the short circuited Warburg finite diffusion element.

\[ \chi^2 = \sum \frac{(observed - calculated)^2}{calculated} \]  

(3.14)

The reproducibility of the CB6 Nyquist plots is shown in all of the resistance values calculated from the equivalent circuit. A means ANOVA of the calculated resistances does not provide separation due to the large variation of the carbon black with lower Raman values. Figure 3.25 shows a plot of the resistances as a function of La for the carbon electrodes. The mean resistance is plotted along with the 95% confidence interval. The solution resistance is consistent amongst the electrode types. The variability is higher for CB1 and CB2, but overall, the solution resistance (Fig 3.25a) is equivalent between electrode types. The source of the solution resistance arises from cell components such as the separator, spacers, springs, and cell casing.
Therefore, the expectation is that the resistance due to cell components would not be related to the carbon type used for the electrode. The bulk resistance (Fig 3.25b), is related to the resistance in the bulk electrolyte solution in the coin cell. Bulk resistance is not expected to correlate to carbon type similar to the solution resistance case.

Figure 3.24 Nyquist and Bode plots from equivalent circuit simulation, a-b) CB1, c-d) CB2, e-f) CB6
The electrode interfacial resistance, R3 (Fig 3.25c) shows a statistically significant difference between CB1 and all of the carbon electrodes. A means ANOVA is shown in Figure 3.26 for the interfacial resistance. The mean resistances, for electrodes made with heat treated carbon, do not statistically separate. According to Kang, the interfacial resistance is a combination of the charge transfer resistance and the adsorption resistance. The interfacial resistance can be used to evaluate the electrode surface between carbons. The separation between CB1 and the heat treated carbons, in terms of the interfacial resistance, supports the hypothesis that heat treatment of carbon provides a more stable surface.

The constant phase element, CPE2 (from Table 3.3) is related to the double layer capacitance at the electrode electrolyte interface. An examination of the exponent, n2, for CPE2 shows that for CB6, the behavior is nearly that of a capacitor. As n2 approaches a value of 1, the impedance for the constant phase element approaches that of a capacitor. The impedance of a Constant Phase Element has been related to surface roughness\textsuperscript{28-29} of an electrode. Recall the impedance of a CPE is given in Equation 3.8.

\[
Z = \frac{1}{Q^0(j\omega)^n}
\]  

(3.8)

where \(Q^0\) is the admittance when \(\omega = 1\) rad/s, \(w\) is the frequency in rad/s, \(j\) represents (-1)\(^{1/2}\), and \(n\) is related to the depression of the semi-circle in the Nyquist plot. The impedance for a single CPE would be a straight line, Q, that makes an angle of \(n\times90^\circ\) with the imaginary axis in the Nyquist plot. The fractal dimension of an electrode surface can be calculated using Equation 16

\[
n = \frac{1}{D-1}
\]  

(3.16)
where \( n \) is the exponent from Equation 3.15 and \( D \) is the fractal dimension. The surface of carbon black is known to be fractal\(^{30} \). Gas adsorption measurements\(^{31} \) are typically used to measure the fractal dimension of a surface. Small angle x-ray scattering\(^{32} \) can also be used to determine the fractal dimension of a rough surface. The carbon electrode surface should exhibit a fractal dimension very near that of the carbon black itself. Untreated carbon black powder should have a fractal dimension close to \( 2.2^{30} \). As the carbon surface is heated, the fractal dimension is expected to decrease closer to an ideal smooth surface, \( D=2.0 \).

### Table 3.5 Fractal Dimension for Carbon Electrode

<table>
<thead>
<tr>
<th>Carbon</th>
<th>( D )</th>
<th>( RSD ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB1</td>
<td>2.16</td>
<td>4.3</td>
</tr>
<tr>
<td>CB2</td>
<td>2.23</td>
<td>2.1</td>
</tr>
<tr>
<td>CB3</td>
<td>2.06</td>
<td>0.4</td>
</tr>
<tr>
<td>CB5</td>
<td>2.06</td>
<td>0.6</td>
</tr>
<tr>
<td>CB6</td>
<td>2.04</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 3.5 summarizes the calculated fractal dimension, \( D \), for the carbon black electrodes. The values compare well with those produced by Zerda\(^{30} \) and Xu\(^{31} \). The variability in the fractal dimension is similar to that observed with the resistance values calculated for the carbon electrodes. The variability exhibited by the untreated surface is not surprising given no modifications have been made to homogenize the surface.
Figure 3.25 Plot of resistances from equivalent circuit impedance model (Equation 3.13) vs. La by Raman a) R1, b) R2, c) R3; error bars represent 95% confidence interval
3.3.5 EIS of Extended Cycle Carbon Electrode

The impedance response was measured for the CB6 electrode that was cycled 50 times (Fig 3.12). The impedance was measured after 5, 10, 20, and 50 cycles were completed. The equivalent circuit model corresponding to Equation 3.13 was used to evaluate the CB6 electrode impedance as a function of time. The goal of this experiment was to predict the growth of the CEI layer on the surface of the electrode.

The values obtained for the simulated impedance were in agreement with the individual coin cells cycled 3 times. The constant phase elements, CPE1 and CPE2, that correspond to bulk and double layer capacitances show a statistically significant relationship with time (Figure 3.27). The bulk capacitance has a logarithmic relationship with cycle time. A sharp rise in the CPE1 value happens during the first 20 cycles. The capacitance between cycle 20 and 50 approaches a steady value. CPE2 shows a quadratic relationship with time. The first 20 cycles
show little change in the double layer capacitance behavior, but after cycle 20, CPE2 begins to increase at a rapid rate. The two constant phase elements appear to be showing two processes.

![Plot of circuit elements versus time for CB6 coin cell cycled 50 times from 2.5V to 5.1V](image)

**Figure 3.27** Plot of circuit elements versus time for CB6 coin cell cycled 50 times from 2.5V to 5.1V a) CPE1 vs. time, b) CPE2 vs. time, c) B vs. time; Regression fit statistics given for each plot

that may correlate. During the first 20 cycles, capacitive behavior increases in the bulk up to a point. Since PF$_6^-$ intercalation is quasi-reversible, the replenishment of the electrolyte salt in the bulk will begin to decrease. At the same time, the PF$_6^-$ becomes trapped near the electrode surface which could result in an increased capacitance in the double layer. The B coefficient, related to the bounded Warburg element, also shows a logarithmic relationship with time. The thickness of the double layer can be calculated from the B constant of the bounded Warburg element using Equation 3.17.
\[ Z_{W} = \left( \frac{1}{\sqrt{2Y_{0}}} \right) \coth(B\sqrt{j\omega}) \]  \hspace{1cm} (3.17)

where \( Y_{0} \) is related to the Warburg coefficient, \( \sigma \), by Equation 3.18, \( \omega \) is the frequency, \( j \) is \((-1)^{1/2} \), and \( B \) is associated with the thickness of the diffusion layer and the diffusion coefficient by Equation 3.19.

\[ \sigma = \frac{1}{(\sqrt{2}Y_{0})} \]  \hspace{1cm} (3.18)

\[ B = \frac{\delta}{\sqrt{D}} \]  \hspace{1cm} (3.19)

where \( \delta \) is the diffusion layer thickness on the electrode, and \( D \) is the diffusion coefficient.

Equation 3.19 was used to calculate the thickness, \( \delta \), for the CB6 electrode at each cycle interval. The value for the diffusion coefficient determined from the CV scans \( (2.58 \times 10^{-10}) \) was used in the calculation of \( \delta \). Table 3.6 summarizes the results of the thickness calculations. The coating thickness increases by approximately 45% from cycle 5 to cycle 50. The thickness of the layer will impact diffusion of de-intercalated \( \text{PF}_{6}^{-} \) back into the bulk electrolyte.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>time (min)</th>
<th>B</th>
<th>( \delta ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>43</td>
<td>0.6103</td>
<td>98.0</td>
</tr>
<tr>
<td>10</td>
<td>87</td>
<td>0.6700</td>
<td>108</td>
</tr>
<tr>
<td>20</td>
<td>173</td>
<td>0.7549</td>
<td>121</td>
</tr>
<tr>
<td>50</td>
<td>434</td>
<td>0.8795</td>
<td>141</td>
</tr>
</tbody>
</table>

The growth of the layer is logarithmic, so as the number of cycles increases, the layer will slowly grow in thickness until very little change occurs between cycles. By extrapolation, the layer
thickness, $\delta$, will continue to grow by 1 nm or more until the number of cycles is greater than 220, which represents approximately 32 hours of cycling.

3.4 Conclusion

Cyclic voltammetry and Electrochemical Impedance Spectroscopy were conducted on carbon electrodes made from the heat treated carbon black series. For the untreated carbon black electrode the CV scan was mainly featureless. A small anodic peak was observed which is likely due to establishment of the CEI at the carbon electrode. The heat treated carbon electrodes exhibited a few additional features in the CV scan. A more distinct peak at 4.25 V (vs. Li/Li+) was identified as being due to either water adsorbed on the carbon black or a rearrangement of binder upon heating the electrode prior to use. Anion intercalation is observed as the carbon black becomes more graphitized by heat treatment. The diffusion coefficient estimated for the CB6 electrode is significantly less than the literature values, which may indicate starvation of electrolyte in the cell.

The equivalent circuit used to model the carbon electrode was consistent with the dual carbon model from both Kang and Kwon. Interfacial resistance was observed to be different in the untreated and heat treated carbons. The variability between coin cells of the same carbon was reduced significantly for the heat treated carbons particularly for CB6. The lower variability was observed for the impedance plots and in the circuit elements determined from the model fits.

The coating thickness was estimated on the extended cycle CB6 electrode. The coating layer grows logarithmically versus cycle time. The growth of the layer may explain the change in capacitive behavior observed as cycle time increased for the CB6 cell. The information
gathered from the carbon electrode will be used in evaluation of high voltage spinel-carbon cathodes.


Chapter 4  Conductive Carbon/High Voltage Spinel Electrodes

4.1 Introduction

The CV and EIS work on the carbon electrode provided some information on the stability of heat treated carbon black in a lithium ion coin cell. The impact of the carbon black needs to be evaluated using an electrochemically active cathode powder that operates at a high voltage. The cathode powder chosen was a mixed stoichiometry spinel, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO). The 5 V LNMO cathode powder was chosen because of the observed cycle stability the material has exhibited in past studies$^1$.

LiMn$_2$O$_4$ was studied for use in lithium ion batteries. The non-doped spinel was expected to provide improved power density, lower costs, and reasonable safety versus the LiCoO$_2$ cathode material that controlled the market. Unfortunately, LiMnO$_4$ suffers from severe capacity fade with extended cycling. The cause of capacity fade was determined to be from dissolution of Mn$^{2+}$ from a disproportionation reaction$^2$ and Jahn-Teller distortion of the spinel structure upon deep discharge$^3$. By introducing another transition metal into the spinel structure, the capacity fade was found to be reduced significantly$^{3-6}$. The introduction of Ni into the spinel structure moved the operating potential up to 4.7 V. The Ni participates in the oxidation-reduction chemistry, which allows the Mn$^{4+}$ to remain undisturbed in the spinel structure$^5$.

Two carbons, CB1 and CB6, were chosen for use in the LNMO experiments. The stability difference between the two carbons will provide a reasonable comparison for the impact of heat treatment of the carbon on the cathode performance. A combination of CV and EIS
experiments were completed to see the initial state of the cathode, and then charge-discharge cycling was conducted to evaluate the impact of the conductive carbon on capacity. The evaluation of the LNMO-carbon electrode performance will also be monitored via *in operando* Raman studies. Due to challenges with the instrumentation and the function of the *in operando* cell, the Raman work for the LNMO-carbon battery cells is still in progress. Raman studies will provide information about how the carbon \(^7-^9\) itself changes with increased charging and discharging, as well as changes to the LNMO itself.

4.2 Experimental

4.2.1 LNMO-Carbon Electrode Paste

The recipe for the electrode paste, by mass, consisted of 40% LNMO, 4% carbon black, 3% PVDF, and N-methylpyrrolidone as the balance. The final dried electrode contained approximately 86% LNMO, 8% carbon black, and 6% PVDF binder. The paste was mixed for 30 minutes using the SPEX mill with a single tungsten ball bearing to assist with dispersion of the dry components in the paste.

Basic analytical characterization of the cathode powder (e.g. surface area, mean particle diameter, and capacity) is summarized in Table 4.1. The analytical characterization of the carbon black powders can be found in Table 3.1. SEM images of the casted electrodes were collected for qualitative inspection of the carbon black distribution amongst the cathode powder. Figure 4.1. The carbon black appears to be evenly distributed amongst the cathode powder, such that good conductivity would be expected for each cathode. The difference in particle size and shape between the LNMO cathode material and carbon black is clearly evident in the SEM images.
Table 4.1 Characteristics of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Cathode Powder

<table>
<thead>
<tr>
<th>Measurement</th>
<th>LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET SA (m$^2$/g)</td>
<td>0.68</td>
</tr>
<tr>
<td>D50 ($\mu$m)</td>
<td>6.3</td>
</tr>
<tr>
<td>mAh/g @C/5</td>
<td>120-125</td>
</tr>
</tbody>
</table>

Figure 4.1 SEM image of LiNi0.5Mn1.5O4-carbon black electrodes a) CB1, b) CB6
4.2.2 Spinel-Carbon Coin Cells

Coin cells were assembled similar to the carbon electrode cells. A 2032 style coin cell was used for the experiments. Lithium foil was used as the reference and counter electrode in the coin cells. The electrolyte consisted of 1M LiPF6 in a 1:1:1 mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate. The assembly of the coin cell is provided in Chapter 3 (Fig. 3.5).

4.2.3 Electrochemical and Charge-Discharge Measurements

Cyclic voltammetry and Electrochemical Impedance Spectroscopy measurements were conducted using the same equipment discussed in Chapter 3. The charge-discharge cycling was completed using the Arbin BT2000 battery testing unit utilizing the MITS Pro software package. Charge-discharge cycling experiments were all conducted at approximately 21°C.

4.3 Results and Discussion

4.3.1 Cyclic Voltammetry of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$-Carbon Electrodes

Cyclic voltammetry scans were collected for each electrode in order to give each cell an equivalent starting point prior to charge-discharge cycling. The CV scans for spinel electrodes with CB1 or CB6 are shown in Figure 4.2. A qualitative assessment of the CV scans was taken for each coin cell tested.

Two peaks are visible in the CV scans of both electrode types. The first is observed at approximately 3.6 V (vs. Li/Li+), while the second peak arises at approximately 4.5 V (vs. Li/Li+). Each cell was subjected to two CV scans from 2.5 V to 5.1 V to condition the cell. For
the carbon electrodes, the difference in currents between the anodic and cathodic scans was not surprising since the carbon black surfaces were changed by the heat treatment. A large difference for the LNMO cathodes was not anticipated since the electrodes were made up of 86% cathode powder by weight. The mass of electrodes containing CB6 was found to be significantly larger than that of CB1. The normalization of capacity by mass of the electrode was expected to account for the difference in electrodes. However, the CV scans indicated that the mass may have introduced an unaccounted for change to the experiment.

![Cyclic Voltammetry](image.png)

**Figure 4.2** Cyclic Voltammetry of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-carbon black electrodes a) CB1 b) CB6

### 4.3.2 Electrochemical Impedance Spectroscopy of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-Carbon Electrodes

Electrochemical impedance measurements were completed for each coin cell before and after cyclic voltammetry, as well as after charge-discharge cycling. The coin cell was allowed to return to open circuit potential prior to collecting EIS measurements after charge cycling experiments.
The Nyquist plot for spinel electrodes with CB1 and CB6 are shown in Figure 4.3. Electrodes for each type of carbon exhibited two semi-circles in the Nyquist plot. The magnitude of the semi-circle differed between the two carbons. At first inspection, the differences in the impedance response could be associated with the carbon difference. Significant variability was observed for both carbon types, but the repeatability appeared to be much smaller for CB6. The response on the real impedance axis is much smaller for CB6 than for CB1 which is consistent with the observations of the carbon electrode alone. Figure 4.4 provides a comparison of the impedance response for CB1-spinel and CB6 spinel electrodes. Equivalent circuit modelling is necessary before drawing too many conclusions regarding the impedance data.
Figure 4.3 Impedance measurements after cyclic voltammetry conditioning a) CB1 + spinel, b) CB6 + spinel; Replicate coin cells represented by separate colors in impedance plots for each carbon type
4.3.3 **Charge-Discharge Cycling of LiNi_{0.5}Mn_{1.5}O_{4}-Carbon Electrodes**

The capacity for the LNMO spinel cathode material has been reported in a range from 120 to 150 mAh/g\(^4,6,10\). Coin cells were subjected to charge and discharge cycling at rates of C/2 and 1C for both carbon types. Figure 4.5 shows a plot of voltage versus discharge capacity of the CB1 spinel electrode through 10 cycles at a rate of C/2. LNMO-carbon electrodes plateau at 4.7 V (vs. Li/Li+) as shown in Figure 4.5. The maximum discharge capacity at C/2 rate was 162 mAh/g, which is in agreement with the values reported in the literature. After 10 cycles the discharge capacity had decreased to 144 mAh/g which represents an 11% drop. A comparison of C/2, 1C, and 2C rates for CB1 spinel electrodes is given in Figure 4.6. As expected, the maximum discharge capacity is lower for higher rates of discharge. In addition, the capacity
fade is larger at increased discharge rates. The discharge capacity is summarized for CB1 spinel electrodes in Table 4.2.

![Figure 4.5 Discharge Capacity of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-CB1 Electrode at C/2 rate](image)
Figure 4.6 Comparison of LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}-CB1 Electrode by discharge rate

The capacity fade is shown in Figure 4.7 over the first 10 cycles for discharge rates of C/2, 1C, and 2C.
Figure 4.7 Discharge cycling characteristics for LiNi_{0.8}Mn_{1.2}O_4-CB1 electrode; Cycling rates of C/2, 1C, and 2C included in plot
The voltage vs. discharge capacity plot for CB6 spinel electrodes is shown in 4.8 for both C/2 and 1C rates. A striking difference was observed in the maximum capacity between the CB6 and CB1 containing electrodes. The potential plateau for CB6 spinel electrodes was at 4.7 V just as in the CB1 case. The maximum discharge capacity was at 125 mAh/g for both C/2 and 1C rates, which is well below that of the CB1 electrodes at the same rate. In addition, no change in the discharge capacity was observed as a function of the rate. The capacity remains equivalent for both the C/2 and 1C rates (Figure 4.9). Although the capacity remains within the reported range, it is unusual to have such a low response. It may be that the additional mass from the CB6 spinel electrode impacted the discharge capacity. Revisiting the discussion from Chapter 3 on electrolyte starvation, the additional mass of carbon in the electrode may have impacted the amount of electrolyte available for operation of the coin cell. The argument against the electrolyte starvation explanation is that the capacity does not fade significantly with cycle

### Table 4.2 CB1-LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Electrode Discharge Capacity by Cycle Number

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>2C Rate</th>
<th>1C Rate</th>
<th>C/2 Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Discharge Capacity (mAh/g)</td>
<td>%</td>
<td>Discharge Capacity (mAh/g)</td>
</tr>
<tr>
<td>1</td>
<td>109</td>
<td>100</td>
<td>137</td>
</tr>
<tr>
<td>2</td>
<td>101</td>
<td>93.5</td>
<td>132</td>
</tr>
<tr>
<td>3</td>
<td>97</td>
<td>89.1</td>
<td>130</td>
</tr>
<tr>
<td>4</td>
<td>95</td>
<td>87.7</td>
<td>129</td>
</tr>
<tr>
<td>5</td>
<td>93</td>
<td>85.5</td>
<td>127</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>82.9</td>
<td>125</td>
</tr>
<tr>
<td>7</td>
<td>87</td>
<td>80.5</td>
<td>123</td>
</tr>
<tr>
<td>8</td>
<td>86</td>
<td>79.0</td>
<td>121</td>
</tr>
<tr>
<td>9</td>
<td>84</td>
<td>77.7</td>
<td>120</td>
</tr>
<tr>
<td>10</td>
<td>82</td>
<td>75.8</td>
<td>119</td>
</tr>
</tbody>
</table>
number. In fact, the stability of the CB6 spinel electrode is excellent for the first 10 cycles as can be seen in Table 4.3 and Figure 4.10.

Table 4.3 CB6-LiNi_{0.5}Mn_{1.5}O_4 Electrode Discharge Capacity by Cycle Number

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>1C Discharge Capacity (mAh/g)</th>
<th>%</th>
<th>1C Discharge Capacity (mAh/g)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>128</td>
<td>100</td>
<td>129</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>126</td>
<td>98.4</td>
<td>125</td>
<td>97.3</td>
</tr>
<tr>
<td>3</td>
<td>126</td>
<td>98.7</td>
<td>124</td>
<td>96.4</td>
</tr>
<tr>
<td>4</td>
<td>126</td>
<td>98.5</td>
<td>123</td>
<td>95.6</td>
</tr>
<tr>
<td>5</td>
<td>126</td>
<td>98.5</td>
<td>123</td>
<td>96.0</td>
</tr>
<tr>
<td>6</td>
<td>127</td>
<td>99.1</td>
<td>124</td>
<td>96.4</td>
</tr>
<tr>
<td>7</td>
<td>126</td>
<td>98.6</td>
<td>124</td>
<td>96.6</td>
</tr>
<tr>
<td>8</td>
<td>125</td>
<td>98.0</td>
<td>124</td>
<td>96.3</td>
</tr>
<tr>
<td>9</td>
<td>125</td>
<td>97.8</td>
<td>123</td>
<td>96.0</td>
</tr>
<tr>
<td>10</td>
<td>125</td>
<td>97.6</td>
<td>124</td>
<td>96.1</td>
</tr>
</tbody>
</table>
Figure 4.8 Discharge capacity for LiNi$_{0.5}$Mn$_{1.5}$O$_4$-CB6 electrode a) C/2 rate, b) 1C rate

Although the maximum discharge capacity was well below that observed for the CB1 electrode, the improved stability over the first 10 cycles appears to support the hypothesis that heat treated carbons provide improved stability for lithium ion cathodes. The source of the reduction in maximum capacity will be investigated as part of the future work.
Figure 4.9 Comparison of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-CB6 Electrode by discharge rate
Figure 4.10 Discharge cycling characteristics for LiNi$_{0.5}$Mn$_{1.5}$O$_4$-CB6 electrode; Cycling rates of C/2 and 1C included in plot

4.4 Conclusion

The purpose of this work was to test the hypothesis that heat treatment of carbon black provides a measurable change in the stability of a high voltage cathode for lithium ion battery applications. In order to test the hypothesis, the carbons with the largest difference in crystallite structure change were used in coin cells with the high voltage spinel cathode material.

The stability in terms of capacity fade for CB6-LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrodes seems to support the hypothesis under investigation. Cyclic voltammetry scans point towards possible issues with the CB6 electrode in terms of the depressed current for the cathodic and anodic scans versus CB1-spinel electrodes. The decreased capacity for the CB6 electrode is related to the observations from the CV experiments, but further investigation is needed to clearly identify the root cause. Equivalent circuit modeling of the impedance results may provide the explanation for the decreased capacity as well.
Future work for the spinel electrodes will include in operando Raman experiments. The design of the in operando cell was sound in terms of electrochemical measurements. EIS and CV measurements were performed on previously analyzed coin cells with the original results being produced using the in operando cell. The seal around the sapphire window in the cell caused issues with operation of the cell. An airtight seal was not achieved for several configurations of the cell. Currently, the cell has been modified using a polyester film as the window for Raman measurements. The window is sealed inside a crimped coin cell to avoid the need for an external seal. Work with the in operando cell will be included in future work.

4. Carroll, K. J.; Yang, M.-C.; Veith, G. M.; Dudney, N. J.; Meng, Y. S., Intrinsic Surface Stability in LiMn$_{2-x}$Ni$_x$O$_{4-y}$ (x = 0.45, 0.5) High Voltage Spinel Materials for Lithium Ion Batteries. Electrochemical and Solid-State Letters 2012, 15 (5), A72.
7. Lei, J.; McLarnon, F.; Kostecki, R., In Situ Raman Microscopy of Individual LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ Particles in Li-Ion Battery Composite Cathode. J. Phys. Chem. B 2005, 109, 952-957.
Chapter 5  Microwave Heating of Carbon Black

5.1 Introduction

Heat treatment of carbon black using traditional furnace technology has been shown to be effective in increasing the level of graphitization of the carbon black particle\(^1\). Furnace type heating relies on convection and conduction to heat the carbon black particle. The carbon black is heated from the outside towards the center of the particles, which is the reason that furnace heating reactions are conducted for long times. In order to achieve the desired level of graphitization, long reaction times are needed to ensure the inner layers of the particle has reached the reaction temperature.

Microwave heating has been used to alter the structure of several carbon material types including carbon nanotubes\(^2\), carbon pitch\(^3\), activated carbon fibers\(^4\), and carbon powder\(^5\). Microwaves heat solids by a different mechanism than typical furnace heating approaches. When polar molecules in the liquid state are exposed to microwave energy, the molecules will begin rotating to align the dipole with the electric field. The realignment of the dipole will lag behind the oscillation of the electric field such that the molecule will absorb energy. The absorbed energy is lost as heat to the system. The molecules ability to be polarized when exposed to the electric field is known as the dielectric constant, \(\varepsilon'\). The heat loss is determined by the dielectric loss for the molecule, \(\varepsilon''\). The ability of a material to convert energy from electromagnetic radiation into heat energy is given by the value of tan \(\delta\) (Equation 5.1).

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]  

(5.1)
Larger values of $\tan \delta$ mean that the material can more easily convert electromagnetic energy into heat, which would result in more efficient heating. The rate of temperature rise in a material, average power absorbed, and the depth of penetration are all dependent on the dielectric loss factor as seen in Equations 5.2, 5.3, and 5.4.

\[
\frac{\delta T}{\delta t} = \frac{2\pi \varepsilon_0 \varepsilon' f E_{rms}^2}{\rho C_p} \tag{5.2}
\]

where $\varepsilon_0$ represents the permittivity in a vacuum, $\varepsilon''$ is the dielectric loss for the material, $f$ is the frequency of the electric field oscillations, $E_{rms}^2$ is the electric field strength, $r$ is the density of the material, and $C_p$ is the specific heat capacity of the material.

\[
P_{av} = 2\pi f \varepsilon_0 \varepsilon_{eff} E_{rms}^2 V + 2\pi f \mu_0 \mu_{eff} H_{rms}^2 V \tag{5.3}
\]

where $V$ is the volume of the material, $\mu_0$ is the permeability of free space, $\mu''_{eff}$ is the effective magnetic loss factor, and $H_{rms}^2$ is the root mean square of the magnetic field.

\[
d = \frac{1}{2 \pi f \left( \frac{\mu \mu' \varepsilon_0}{2} \right)^{1/2} \left( \frac{1 + (\tan \delta)^2}{2} - 1 \right)^{1/2}} \tag{5.4}
\]

where $\mu'$ is the relative permeability.

The ability of the material being heated to convert electromagnetic radiation into heat plays a major role in all the relationships given in Eqns 5.1 – 5.4. The frequency of the microwave is limited to 2.45 GHz to avoid interference with telecommunications applications, and commercial microwaves have set field strengths. Other than the inherent properties of the carbon black used in this work, the volume of the material used is the only other handle that can be controlled in the
experimental design. The initial phase of the experimental design did not include volume as a parameter. Future experiments will include the impact of volume on the microwave graphitization of carbon black samples.

5.2 Experimental

5.2.1 Reaction Vessel and Microwave Information

The reaction vessel consisted of three glass pieces. A fritted flask bottom had a 45/50 joint ground glass joint at the top which allowed the glass union piece to fit inside of the fritted-ware. A standard 24/40 top from a gas washing bottle, with the inner stem removed, served as the top piece in the assembly. The argon purge lines were connected to the inlet fitting of the top, and an exhaust line was connected to the outlet fitting. The exhaust line was placed in a fume hood to safely exhaust the argon out of the laboratory. High temperature insulation was placed inside the fritted ware bottom to keep the temperature of the glass pieces below the softening point. A crucible made of fused quartz was used to contain the carbon black during the reaction. The fused quartz crucible has a softening point of > 1700°C which is above the expected temperature of reaction in the microwave. The reaction vessel was purged for 10 min prior to exposure to microwave radiation in order to minimize the oxygen present in the vessel. The volume of the vessel assembly was calculated using an equivalent cylinder. The overestimated volume provides a safety factor for gas volume changes to ensure oxygen content is minimized during microwave heating. The volume of the vessel assembly was estimated at 0.27 L. At a rate of 2 L/min, the number of volume changes of gas in the assembly was 75 after 10 minutes. The argon purge was applied throughout the microwave heating and sample cooling stages.
A commercially available laboratory microwave system (Milestone Ethos, Milestone, Inc.) was used for the reactions. The microwave operates at 2.45GHz with a maximum power output of 1000 W. For each experiment, the microwave power was set to 1000W for the duration of exposure time. After the heating was complete, samples were allowed to cool in the microwave cavity with active argon purging. The mass of carbon black used was approximately 1.5g for each experimental run. Two grades of carbon black were used to determine if initial particle morphology limited graphitization during microwave heating.

5.3 Results and Discussion

5.3.1 Crystallite Growth by X-Ray Diffraction with Respect to Microwave Heating Time

The crystallite growth was measured using x-ray diffraction and Raman microspectroscopy as described in Chapter 2. The heating experiments were limited to a maximum time of 1 minute due to limitations with the reaction vessel. The crystallite size in the a and c directions increase with increasing time of exposure to microwave radiation. A plot of $L_c$ and $L_a$, by x-ray diffraction, for sample CB1 is shown in Figure 5.2. The shape of the curve is
similar for both measurements. Growth appears to be steady throughout the first 40 s of heating. Above 40 s, the rate of growth in La and Lc appears to increase.

**Figure 5.2** Crystallite size growth for carbon black CB1 exposed to microwave heating at 1 kW in an argon atmosphere

**Figure 5.3** Crystallite size growth for carbon black CB7 exposed to microwave heating at 1 kW in an argon atmosphere
A linear growth rate is observed in La and Lc for CB7 (Figure 5.3). The change in crystallite size was plotted versus the microwave exposure time for both carbons in an attempt to evaluate the kinetics of growth. The regression plots of ΔLa and ΔLc versus time are shown in Figures 5.4 and 5.5 for CB1 and CB6 respectively. For CB1, both regression lines follow an exponential growth. Initially, the growth perpendicular to the basal plane may lag behind lateral growth for CB1, but the regression fit appears to be approaching a convergence point. The growth in CB7 is linear for both La and Lc. Three growth processes were proposed by Emmerich⁸ for carbons subjected to heat treatment, (1) growth within the plane, (2) growth in the c-direction through coalescence, and (3) growth in the a-direction through coalescence. The third process is not expected to occur in this case as it was proposed to occur at temperatures above 2400°C.

Typical growth in carbon black has been observed as a sigmoidal shaped function of crystallite size versus temperature¹,⁹. The expectation in the microwave experiments was that a similar shaped model would describe the growth. Based on the shape of the regression fits in Figs. 5.4 and 5.5, the growth appears to be entering (CB1) or in the steep rising portion (CB7) of a sigmoidal function. A vessel redesign is needed to proceed further with development model for crystallite growth through microwave heating of carbon black.
Figure 5.4 Regression fit of the change in crystallite size versus time is shown for CB1, La (red squares), Lc (blue diamonds)

Figure 5.5 Regression fit of the change in crystallite size versus time is shown for CB7, La (red squares), Lc (blue diamonds)
5.3.2 *Raman Spectroscopy of Microwave Heated Carbon Blacks*

The samples prepared by microwave heating were analyzed using the Raman microscope. First, a qualitative analysis of the changes to the G and D bands in the Raman spectra were evaluated for each sample. In addition, the Raman method was used to measure the crystallite size, La, for each carbon. The results of the Raman analysis is compared to that of x-ray diffraction presented in the previous section.

The Raman spectra for microwave heat treated CB7 samples are shown in Figure 5.6. The characteristic sharpening of both the D and G bands with increasing heat treatment are observed in the microwaved samples as well. After 30 s of microwave exposure, a definitive G’ band has appeared at approximately 2660 cm\(^{-1}\), and the D and G bands are nearly the same height and width. At 60 s of heating, the intensity of the G band is higher than that of the D band, and additional combination bands have appeared near the G’ band. Graphitization of CB7 has clearly occurred based on inspection of the Raman spectrum for each sample. The process supports the observations from the x-ray diffraction analysis of crystallite size.
The transformation of CB1 with microwave heating is different than for CB7. The progression of graphitization appears to be much slower for CB1. At 60 s of microwave heating, the G’ band is becoming more pronounced in the spectrum, but the intensity of G’ is far below that observed for CB7 at 60 s of microwave exposure. The D and G band are becoming narrower in terms of peak width, and the G band is nearly at the same intensity as that of the D band. The Raman spectra of CB1 show similar growth as that observed with x-ray diffraction measurements.
In order to see the difference in the growth rate between CB1 and CB7, the change in crystallite size versus time at 1 kW of microwave exposure was plotted (Figure 5.8). The regression line for both carbon black types is linear with a reasonable correlation coefficient. The slope for CB1 is approximately half that of the CB7.

The regression line for CB1 appears to be clearly linear, but CB7 data may fit to a logistic function. A logistic function was fit to the crystallite size data to determine if the growth rate kinetic constant could be obtained. Figure 5.9 shows the plot of the logistic function along with the La results for CB7 by Raman. Equation 5.5 was used to fit the La values of CB7 with time,

\[ La(t) = \frac{\Delta L_{max}}{1 + e^{-k(t_i-t_m)}} + La(0) \]  

(5.5)
Where $\Delta L_{\text{max}}$ is the maximum difference from the initial value of $L_a$ for the carbon black, $k$ is the rate constant for growth, $t_i$ represents the time for the $i$th interval, $t_m$ is time at which the maximum growth rate occurs, and $L_a(0)$ is the initial value of the crystallite size for the carbon black. As can be seen in Figure 5.9, the fit of the logistic curve to the $L_a$ measurements for CB7 is reasonable ($R^2 = 0.997$). Parameters for the rate constant and the maximum value of $L_a$ can be predicted from the logistic function fit. However, it is recognized that the number of measurements is too low to claim the full kinetic relationship has been described adequately here. It is likely that the relationship shown in Figure 5.9 represents a local maximum. Further experimentation is needed to fully characterize the kinetic behavior of crystallite growth in carbon black subjected to microwave heating.

**Figure 5.8** Change in crystallite size plotted versus the exposure time to microwave radiation; CB1 (red open squares), CB7 (blue open diamonds)
5.3.3 \textit{La} by Raman vs X-Ray Diffraction for Microwave Heated Carbon Blacks

A few comments must be made regarding the difference in the La values obtained from Raman versus x-ray diffraction. For conduction/convection heat treated carbon black samples, the La values determined by both Raman and XRD were shown to be equivalent. For the microwave heat treated materials, there appears to be a significant discrepancy in the La results. The slope of the La plot vs. time for Raman measurements is almost a factor of 4 larger than for XRD (0.54 vs. 0.14 respectively). A possible explanation lies in the differences between the measurement techniques. Raman micro-spectroscopy is a surface technique in that the penetration depth of the laser at 532 nm is less than 1 \( \mu \text{m} \). X-ray diffraction on the other hand is
an average measurement of the bulk of the sample. The discrepancy could be due to variability between the measurements, or perhaps the graphitization has occurred to an extent that the average measurement by XRD is not effectively picking up the rise in graphitization level. A look at the particles with TEM may provide some insight into the issue.

![Graph showing La measurement for CB7 microwave heat treated carbon black samples, Raman (diamonds), x-ray diffraction (circles)](image)

**Figure 5.10** La measurement for CB7 microwave heat treated carbon black samples, Raman (diamonds), x-ray diffraction (circles)

### 5.3.4 TEM of Microwave Heated Carbon Black Samples

TEM images of the carbons that experienced the highest level of microwave heating were collected to evaluate the growth of graphite layers in the samples. For the case of CB7, the Raman spectrum of the sample subjected to 60 s of microwave heating indicated that growth of the graphite domains in the aggregate should be reasonably advanced. Measurement of La by XRD did not show much growth by comparison.
Figure 5.11 TEM image of CB7 exposed to 1kW for 60 s in an argon atmosphere

The TEM image shown in Figure 5.11 shows that graphitic regions are definitely present in the CB7 sample. The regions are not as ordered as those observed for CB6 (Fig. 2.14). Inspection of additional fields shows variability in the location of the graphitic regions. It is quite possible that the variability in the extent and location of the graphitic domains contributed to the observed difference in the La measurement. Future experiments will include measurements using both Raman and XRD, but TEM analysis should be added to confirm the heterogeneity of the extent of graphitization.
5.4 Conclusion

Microwave heating of carbon black samples was found to be an effective way to graphitize carbon black particles. The mechanism for microwave heating provides localized heating of the solid, which significantly reduces the time and energy consumption for the graphitization. Measurements of crystallite size indicated that growth occurs within the first 15 s of microwave exposure. Limitations in the vessel design did not allow for experiments to go beyond 1 min of heating. Future experimentation will be focused on characterizing the kinetic relationship for microwave graphitization of carbon black.

Discrepancies between XRD and Raman measurements need to be monitored further to concretely identify the cause. The surface nature of Raman micro-spectroscopy may be able to measure heterogeneity on the surface of the graphitized carbon blacks more effectively than XRD. Further investigation using both techniques along with TEM will be necessary.

Chapter 6 Future Research and Conclusions

The use of conductive carbon additives is critical to the performance of cathode materials in lithium ion batteries. The carbon black provides many beneficial properties to the battery performance, but it brings with it characteristics that may contribute to reduction in battery performance as well. Continued research into the surface and structural features that effect high voltage cycling performance will result in the development of conductive carbons that are efficient, cost effective, and provide a higher level of safety in lithium ion batteries.

6.1 In operando Raman Mapping of Electrodes

The challenges experienced with the in operando Raman cell did not allow for results to be included in the current work. Electrochemical measurements with standard 2032 coin cells demonstrated the functionality of the cell, but the weakness was related to the seal of the window material to the cell body. Future experiments will utilize polyester film as the window material sealed within the coin cell body. In using the sapphire window materials, the seal needed to be made external to the cell. The integrity of the window seal to the coin cell body was not solid enough to conduct in operando measurements. A better seal will be achieved with the polyester film installed inside of the coin cell, and the working distance between the sample and the microscope objective will be minimized as well. The carbon electrodes can be mapped to characterize structural changes in the carbon as they are subjected to charge-discharge cycling and constant potential experiments. The mapping studies should provide information on the structure stability, and possibly the intercalation behavior near 5 V for the carbon electrode. In addition, the high voltage spinel electrodes will be mapped using the in operando cell. High voltage
spinel electrodes can be analyzed using the All Reflecting Objective on the micro-FTIR unit while undergoing charge-discharge cycling to understand the growth of the CEI layer on the electrode surface with time and state of charge.

6.2 Microwave Heat Treated Carbon Electrode Performance

The vessel for the microwave heating requires redesign to move towards full graphitization of the carbon black powders. With a more functional reaction vessel, the impact of surface area, structure, and particle size can be fully developed using microwave heating. Next, the carbon black samples will be tested in coin cells similar to the conventional heat treated carbon black samples. A side by side comparison will indicate if microwave heat treatment is effective for making battery grade carbons. Microwave modified carbon black samples should be tested in carbon electrodes and with a variety of cathode materials (e.g. high voltage spinel, LiFePO₄, etc.) to understand the range of applications for which the carbons could be utilized.

6.3 High Voltage Spinel Experiments

The EIS measurements for the high voltage spinel electrodes need to be fully analyzed using the equivalent circuit model approach. The search for the appropriate circuit configuration is currently in progress. Two Randles circuits in series is a possible model to utilize for the high voltage spinel electrodes. The model used for the carbon electrodes did not provide a reasonable fit to either the Bode or Nyquist plots for the spinel. The processes exhibited by the spinel electrode do not appear to be dominated by the presence of the carbon.
A thinner CB6-spinel electrode needs to be prepared and tested to confirm the charge discharge behavior comparable to the CB1 sample. Cyclic voltammetry, EIS, and discharge capacity measurements will be important for finishing the comparison of the carbon impact on the high voltage electrodes.