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Lithium-Ion Battery Anodes of Randomly Dispersed Carbon Nanotubes, Nanofibers, and Tin-Oxide Nanoparticles

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LITHIUM-ION BATTERY ANODES OF RANDOMLY DISPERSED CARBON NANOTUBES, NANOFIBERS, AND TIN-OXIDE NANOPARTICLES

A dissertation submitted in partial fulfillment of the Requirements for the degree of Doctor of Philosophy

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ABSTRACT

Simon, Gerard, Klint, Department of Biomedical, Industrial, and Human Factors Engineering, Wright State University, 2011, Lithium-Ion Battery Anodes of Randomly Dispersed Carbon Nanotubes, Nanofibers, and Tin-Oxide Nanoparticles.

Lithium-ion battery anodes with a nanostructure of randomly dispersed carbon nanofibers (CNFs), carbon nanotubes (CNTs), and nanoparticles of tin-oxide or silicon were fabricated and tested in order to develop high capacity, easily manufactured anodes. In these anodes, a mesh of CNTs and CNFs form a conductive network within which the nanoparticles of tin-oxide are suspended. The CNT network directs electron flow to and from the nanoparticles while accommodating their volume changes. The CNFs were intended to aid electron transport by serving as conduction channels between the CNTs and the current collector. Secondarily, the CNFs reinforce the physical structure of the anodes. The nanostructure of the anodes allows the electrolyte to freely penetrate, facilitating ionic transport. In most cases, the components of the anode were held together by Van der Waals forces. Both single-walled carbon nanotubes and multi-walled carbon nanotubes were used in this study in order to determine if there performance would be similar.

The anodes take advantage of the specific capacity of tin and tin-oxide, which are 981 mAh/g and 1,491 mAh/g, respectively. Because tin is known to expand to three times
its original size when it alloys with lithium, it is used in nanoparticle form for these anodes and thus avoids the tendency of tin to disintegrate.

To achieve the desired nanostructure, processing methods based on buckypaper formation were explored. Sonication processes were experimented with to determine the optimum conditions for the fabrication of the anodes. Additionally, additives to aid in the binding of the tin-oxide nanoparticles to the CNTs were explored. These included the addition of polyvinylidene fluoride (PVDF) or carbonized phenolic resins.

Anodes were found to exhibit the highest reversible capacity when the processing times were kept to a minimum. This was most likely due to the tendency of CNTs to shorten when sonicated. The shorter sonication times were sufficient to allow the desired level of entrapment of the tin-oxide nanoparticles by the CNTs without degrading the physical characteristics of the CNTs. While the CNTs were intended to move with the tin-oxide nanoparticles and maintain electrical contact as they expanded and contracted, it was discovered that a film of electrolyte-based material formed on the nanoparticles, CNTs, and CNFs, disrupting the current flow.

A mechanistic model was developed to illustrate the internal degradation of the anodes. Resistance and reversible capacity prediction models were also developed. The resistance prediction model was used to confirm the effect of the CNFs on the electrical characteristics of the anodes. As its name implies, the reversible capacity prediction model can be used in future endeavors to predict the reversible capacity that may be
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1. INTRODUCTION

1.1. Lithium-ion Batteries

Secondary batteries have become vital in our society, powering a large variety of electronic devices and automobiles. The development of the lithium-ion battery, which is lighter and more energy dense than its predecessors has made many of the new devices possible. Additional uses for lithium-ion batteries in the military and biomedical fields are envisioned, but only if the performance of the batteries are achieved. Some of the properties being sought are better low temperature performance, increased safety, higher charge and discharge rates, increased overcharge tolerance, and of course, greater energy capacity.

In military applications, these benefits will go toward batteries for both piloted and unmanned aircraft, portable devices for ground troops, and energy storage for encampments. In the biomedical field, improvements in lithium-ion batteries will enable more powerful and longer running prosthetics for amputees as well as implantable, rechargeable pacemakers, defibrillators, and spinal cord stimulators which will improve the patients’ quality of life while reducing health care costs. Additionally, one of the most anticipated results of improved lithium-ion batteries will be fully electric vehicles which possess long ranges and fast recharge times. None of these applications will be possible unless there are vast improvements in anode and cathode
capacities and charge/discharge rates, in conjunction with more stable electrolytes that can handle higher levels of energy.

In the cathode area, while lithium-cobalt-oxide (LiCoO$_2$) remains the most widely used material, its safety and cost limitations have forced industry and researchers to turn to alternative materials such as lithium-iron-phosphate (LiFePO$_4$). This cathode material has a higher capacity, potentially lower cost, and will not facilitate combustion when overcharged or shorted.

Anodes have more options for improvement, but many of these methods rely upon the incorporation of materials such as silicon or tin-oxide. Silicon and tin-oxide are often used to increase the anode capacity because they have specific capacities of 4,200 mAh/g and 1,491 mAh/g, respectively [1,2]. Some researchers have developed anodes based on silicon or tin-oxide nanowires, ball-milled nanocomposites of silicon and carbon, carbon-coated silicon, or tin-oxide deposited on functionalized carbon nanotubes [1,3-6]. While these materials function well in laboratories, they have not yet been accepted by industry.

This effort focused on the use of buckypapers, a simple but effective method to combine the constituents of the anode and create a nanostructure, which incorporates three levels of electron transport, one of which also provides structural support. It will be demonstrated that this structure enhances the performance of lithium-ion batteries.

**1.2. Battery Materials**

The purpose of the buckypaper in this effort is to form a carbon backbone which supports silicon or tin-oxide nanoparticles and transports electrons to and from them.
The buckypaper is composed of single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs), laced with carbon nanofibers (CNFs) to improve the anode’s structural integrity.

1.2.1. Carbon Nanotubes

Before beginning a discussion of carbon nanotubes (CNTs), we must first discuss graphene. Graphene is a two-dimensional sheet of sp² bonded carbon atoms [7,8]. The graphene sheet is formed when the number of atoms in a cluster reaches a point where the binding energies of the interior atoms are dominant over the exterior atom binding energies. Therefore, the edge atoms and tendency to curve are less important, causing the formation of two-dimensional sheets [9].

A CNT is a member of the fullerene family and is formed by a single graphene cylinder or multiple concentric, graphene cylinders. CNTs are generally discussed in terms of single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs), respectively. SWNTs are 1.37 nm in diameter, while MWNTs can range from 4 to tens of nanometers in diameter. Both can be several microns long. CNTs are fabricated by a number of methods that include laser ablation of graphite targets, sometimes with a metal catalyst in a reactor [9], arc-discharge of graphite electrodes [10], and chemical vapor deposition using a metal catalyst to initiate CNT growth [10].

CNTs exhibit many interesting properties, such as extremely low resistivity, high thermal conductivity, and high strength. These characteristics have led to extensive studies to include them in composites for applications ranging from structural to
thermal protection. For lithium-ion batteries, CNTs have also demonstrated interesting properties. These will be discussed in more detail in successive chapters.

1.2.2. Carbon Nanofibers

Carbon nanofibers (CNFs) are vapor grown relatives of CNTs with a notable difference. Unlike CNTs, which are single or concentric graphene cylinders, the graphene planes in CNFs are canted and form a “stacked cup” structure, which in battery applications creates defects which may trap lithium. CNFs possess good electrical and thermal properties. Its resistivity has been measured at $5 \times 10^{-5} \, \text{ohm-cm}$, and in composites CNFs have been shown to increase thermal conductivity 14X [11]. In this research, the tensile strength of CNFs and their ability to reinforce the anode materials is of importance. CNFs have been shown to more than triple the Young’s modulus of nylon composites [10].

1.2.3. Silicon Nanoparticles

Of all the materials that can be used in lithium-ion batteries, silicon possesses the greatest ability to alloy with lithium. When alloyed with lithium, it forms a phase which consists of $\text{Li}_{22}\text{Si}_5$. According to Equation 1, this yields a theoretical capacity of 4,200 mAh/g. However, when silicon alloys with lithium, its volume increases up to 400%, making it a difficult material to integrate into batteries [12]. In bulk or thin-film form, the expansion and contraction of silicon as it alloys and de-alloys with lithium causes it to pulverize and lose reversible capacity. This is the primary reason for using silicon in nanoparticles form.
To gain the full benefit of using silicon, the anode fabrication process must be modified to limit the amount of oxygen exposure to the nanoparticles and nanoparticle-enhanced anodes. Because of this, the experiments in this research were conducted using tin-oxide as a substitute for silicon.

1.2.4. Tin-oxide Nanoparticles

The theoretical capacity of tin-oxide is the third highest, after silicon and germanium, among the anode constituent materials. Applying Equation 1 to tin-oxide’s atomic weight yields a theoretical capacity of 1,491 mAh/g [2]. After the first cycle, when the oxygen in the tin-oxide is irreversibly bound to lithium, tin’s theoretical capacity comes into effect at 981 mAh/g. There is a 34% loss of capacity in the tin-oxide regardless of anode composition or fabrication strategy. Like silicon, tin-oxide’s volume increases when it alloys with lithium, up to 300%. Therefore, it is also subject to pulverization when used in bulk or thin film form. Tin-oxide was used in this effort because no extra controls would be necessary to protect the nanoparticles from the atmosphere.

1.3. Randomly Dispersed SnO$_2$-CNT-CNF Anodes

The three constituents of the anodes are silicon or tin-oxide nanoparticles, CNTs, and CNFs. Because silicon oxidizes, tin-oxide was used for this research. The tin-oxide nanoparticles are the primary source of capacity in the anode. As previously discussed,

\[
\text{Capacity} = \frac{96485 \text{ Coulombs} \cdot \text{mol}^{-1}}{(\text{Si Atomic Weight} \cdot \text{Si/Li ratio})} \quad \text{Equation 1}
\]

\[
\text{Capacity} = \left[\frac{96485 \cdot (1000/3600)}{28.09 \cdot (5/22)}\right]
\]
the tin-oxide nanoparticles will grow and shrink as they alloy and de-alloy with lithium. Therefore, the function of the CNTs is to hold and maintain contact with the nanoparticles throughout their volume changes while contributing to the capacity of the anode. The CNFs were envisioned to be beneficial to the capacity of the anode by functioning as current collectors for the CNTs, which in turn perform electron transport for the tin-oxide. Together, the three materials form a three-dimensional, nanostructure that is theorized to produce excellent electrochemical performance, in excess of currently available materials.

1.4. Research Objectives

The objective of this research is to investigate methods to incorporate silicon and tin-oxide nanoparticles into a lithium-ion battery anode and accommodate their tendencies to expand and contract. To accomplish this, several steps were necessary:

- Identify a nanostructure that provides good retention of the nanoparticles and promotes high ionic and electronic transport throughout the anode.

- Develop a process for acquiring the necessary nanostructure.

- Characterize anode samples to determine the efficacy of the fabrication process.

- Determine characteristics of the anodic structure that contribute or detract from the anodes’ performance.

- Construct models to predict the behavior and performance of the anodes.
The approaches to complete these tasks are presented in this dissertation, along with the experimental results. When these tasks were completed, the results of the experiments were used to determine if:

1. Nanoparticles will be the primary lithium storage media
2. The CNTs will transport electrical current to and from the nanoparticles.
3. The CNTs will remain in contact with the nanoparticles and accommodate their volume changes.
4. MWNTs will function as well as SWNTs in the anodes.
5. The CNFs will facilitate electron transport from the CNTs to the current collectors of the cell.

1.5. **Dissertation Overview**

The work has been presented in five parts:

1. A discussion of the characterization techniques used throughout the research (chapter 3).
2. The discussion of the fabrication process and electrochemical testing method for the anodes (chapter 4).
3. The study of the nanostructure and electrochemical properties of the anode constituents (chapters 5 to 9).
4. The study of the nanostructure and electrochemical properties of the test anodes (chapter 10).

5. The discussion of models used to predict the breakdown of the anodes, estimate anode resistance, and estimate the reversible capacity (chapter 11).
2. LITERATURE REVIEW

2.1. Introduction

Lithium-ion technology has revolutionized the battery industry and made numerous miniaturized electronic devices possible. The success of hybrid and electric vehicles in development also depends on the Li-ion battery. The low weight and high capacity of this battery chemistry are key enablers to longer range and lower operating costs in the auto industry as well as the aerospace industry. In the biomedical industry, these same features will contribute significantly to the quality of life of prosthetic wearers and users of cochlear implants and spinal cord stimulators. They will also enable the implementation of ground-breaking devices such as rechargeable pacemakers[13].

2.2. Anode Materials

The anode is the battery component that contributes most to the battery performance as far as capacity is concerned. Increases in anode specific capacity translate directly into increases in the total capacity of the battery. Research efforts demonstrate possible capacity boosts of 3 to 10 times the current anode specific capacity.

2.2.1. Nano-Sized Carbon Based Anode Materials

In the interest of increasing the capacity of lithium-ion batteries, the anode is being heavily researched. It is graphite based in current batteries and intercalates lithium well with a theoretical specific capacity of 372 mAh/g. It is also inexpensive and widely
available. This limit on the specific capacity is partially imposed by the thermodynamic equilibrium saturation composition of LiC₆ [14,15]. In practice, one can expect to attain a reversible capacity in the vicinity of 350 mA h g⁻¹[16-18]. However, research efforts have demonstrated that anode capacity boosts of 3 to 10 times what is currently available will be possible in the near future.

Carbon nanotubes (CNTs) are a large part of the anode material research. While CNTs are materials of interest to unlock new capabilities in a variety of fields, in battery technology they are mostly being developed to increase the specific capacity of anodes. CNTs are producing very interesting results.

Raw unprepared multi-walled carbon nanotubes (MWNTs) have shown a fairly low reversible capacity ranging from as low as 175 mAh/g to 237 mAh/g [19,20] at a rate of 30 mA/g. These are CNTs with diameters between 4-50 nm and lengths of several microns. They are also often capped, possibly limiting their intercalation abilities. Once the caps of MWNTs are removed by oxidation treatment in air, the reversible capacity improves to 625 mAh/g [20]. This is attributed to lithium intercalation directly into the CNT cores [17,21].

As grown single wall carbon nanotubes (SWNTs) have achieved a reversible capacity of 450 mAh/g, exceeding the capacity of graphite [14]. Purification of the nanotubes is a simple and effective step to remove non active materials and improve the total specific capacity of the material. After purification to 80% purity by filtering the materials through a micro-pore membrane, the SWNTs’ reversible capacity increased to 600 mAh/g after the first cycle, while the irreversible capacity was 1,600 mAh/g. Finally, a
1,000 mAh/g reversible capacity was achieved on the first cycle by ball milling the SWNTs [21]. In this example, the irreversible capacity was 700 mAh/g (1,700 mAh/g total capacity). After the second cycle, the total capacity dropped to 1,000 mAh/g for a 700 mAh/g loss of capacity. Ball milling the SWNTs breaks the tubes and exposes the edges of the graphene layers to which lithium can intercalate itself. Ball milling also increases the surface area of the CNTs, allowing more lithium to intercalate. The lithium is not easily de-intercalated and the irreversible capacity increases. These SWNTs were produced by pulsed laser ablation of a graphite target [21,22]. Swagelok-type cells [23], without polymer binders or carbon black, were used with Li foil and nanotube films for electrodes. The cells were charged and discharged at a rate of 50 mA/g.

Another method of pushing the capacity of CNTs beyond that of the raw product is by acid etching. Acid etching has the effect of shortening the MWNTs and creating defects in the MWNT surface. This increases the surface area of the CNTs and creates additional intercalation sites. After purifying and etching, MWNTs, achieved a reversible capacity of 597 mAh/g for a 20 hour etch and 681 mAh/g for a 10 hour etch [24]. These results come with high irreversible capacities (1,229 mAh/g for a 20 hour etch). The electrochemical tests were performed at a rate of 50 mA/g. These MWNTs were made by a thermal chemical vapor deposition (CVD) method [24-26], purified to 95% purity in HF acid and distilled water for 18 hours, and gas-phase oxidized in a 15% air/Ar mixture at 550°C for 1 hour. After sonication in concentrated HCl acid (37%) for 10 minutes, the MWNTs were filtered and dried. Acid etching was accomplished in a 3:1 ratio of concentrated H2SO4 acid (96%) and HNO3 acid (70%) for 5-20 hours [24]. While one may
expect to increase the reversible capacity by creating more defects, the opposite may also be true. In the work discussed here, the 10 hour etched CNTs actually had a better capacity than the 20 hour etched CNTs. The irreversible capacity was also higher for the 20 hour etch, indicating that lithium is not easily removed from the artificially created intercalation sites. Therefore, defect creation increased the total capacity at the expense of reversible capacity.

The CVD MWNTs were 10-20 nm in diameter and over 10 µm in length, and the AE MWNTs were 2-20 nm in diameter and over 1 µm in length with closed ends. Chemically etching and sonicating the CVD MWNTs reduced the MWNT lengths to 0.2 to 2 µm with the ends opened [24]. While no charge or discharge rate was given for this work, we can still see that etching the MWNTs can create defects in the MWNT sides (additional intercalation sites for lithium), increasing the capacity. This correlates with assertions that lateral defects in the MWNTs allow for lithium intercalation, possibly by creating fractures in the graphite layers [27,28]. However, the creation of locations in the CNT structure for intercalation also brings the risk of significantly increasing the irreversible capacity.

Buckypapers, on the other hand, use as grown purified or unpurified nanotubes, and are more focused on developing an easy to fabricate, lower cost (than processed CNTs), but high performing anode. The nanotubes are normally dispersed by ultrasonication and vacuum filtered through membranes of polyvinylidene fluoride (PVDF), cellulose, poly(tetrafluoroethylene), or similar materials to form a self-standing mat which is dried for 12-24 hours. Several solvents may be used for dispersal and they include Triton X-
100, acetone, water, and n-methylpyrrolidone (NMP), among others. Buckypapers may also be made directly from reflux solutions following acid reflux purification [29]. After several cycles, the reversible capacity of SWNT papers has been found to range from 175 mAh/g for 95% pure SWNTs tested with an ethylene carbonate (EC):dimethyl carbonate (DMC) electrolyte [29,30] to 520 mAh/g for high purity SWNT papers tested with an EC:propylene carbonate (PC):DMC electrolyte [29]. While the use of PC in the electrolyte may lead to increased capacity, it is known to cause exfoliation of graphene layers in graphitic carbons [31,32]. Multi walled carbon nanotube buckypapers were found to have a reversible capacity range from 150 mAh/g to 225 mAh/g after 20 cycles at a C/5 rate [33]. Again, the performance depended upon the electrolyte being used with the EC:PC:diethyl carbonate (DEC) electrolyte providing the best performance. The performance of the buckypaper anodes was not sufficient for them to become a serious competitor to graphite. While the use of CNTs greatly increases the surface area of the anode, the SEI formation is also increased and this results in the trapping of more lithium ions and higher irreversible losses. The irreversible losses of the SWNT papers were as high as 400 mAh/g, while the MWNT papers’ losses were as high as 340 mAh/g [29,33]. Compare these values to graphite’s irreversible capacity of 22 mAh/g [16-18].

Graphene sheets, two-dimensional layers of carbon atoms, are also being studied as potential anode components for lithium-ion batteries. While the graphene sheets are normally stacked in numerous layers when found in graphite form, they appear to offer greater performance when used in very few layers. Four layers of graphene sheets, approximately 2.1 nm thick were prepared by oxidation and rapid thermal expansion of
graphite powder. After 40 cycles, this material was still capable of producing a reversible capacity of 848 mAh/g at a rate of 100 mA/g [34]. This compares well to the results obtained from graphene sheets that were produced by exfoliation of graphite crystals, and were 6 to 16 layers thick. These sheets were only able to produce a 240 mAh/g reversible capacity also at a rate of 100 mA/g [35]. With these results, we may assume that minimizing the number of layers in graphene sheets may be beneficial to anode performance in lithium-ion batteries. The loss of efficiency with increasing number of layers may be a result of the formation of the SEI, which increases with more layers, and the trapping of lithium ions, which also increases.

2.2.2. Nanowires

Nanowires of silicon, germanium and tin-oxide are interesting candidates for Li-ion battery anodes because of their ability to alloy with large amounts of lithium. Their theoretical capacities are among the largest at 4,200 mAh/g for silicon [1], 1,625 mAh/g for germanium [12,36], and 1,491 mAh/g for tin-oxide (SnO₂) [2]. Problems arise when these materials are used in their bulk forms. They experience large changes in volume during lithium insertion and de-insertion [12,37], 400% for silicon and 370% for germanium, for example. The large volume changes lead to pulverization, capacity fade [1,38], and loss of electrical contact in the electrodes [1,39]. The use of nanowires allows the materials to undergo facile strain relaxation, expanding freely radially and axially, consistent with prior work which indicated that particles small in size (micro or nanoscale) will not fracture any further [1,40,41].
Silicon nanowires grown directly onto stainless steel substrates (Figure 1) using the vapor-liquid-solid template-free growth method [42-45], were capable of a 3,193 mAh/g reversible capacity (irreversible capacity of 1,084 mAh/g) over 10 cycles [1]. This was with a C/20 rate and there is some reduction in capacity with increased rates. At the 1C rate, the reversible capacity drops to 2,100 mAh/g (irreversible capacity of 2,177 mAh/g). This still far exceeds graphite’s reversible capacity. The average diameter of these nanowires increased from 89 to 141 nm after lithiation. While the nanowires shrink in size when de-lithiating, they do not normally return to their condition. One can infer that there must be some detachment of the nanowires from the substrate since it is well known that degraded electrical contact between the silicon and the rest of the anode is a large contributor to capacity loss. For improved performance, a two phase nanowire was proposed to reduce the irreversible capacity of nanowires.

A silicon nanowire anode material with a crystalline core and an amorphous shell was developed and grown by CVD to exploit the superior cycling performance of amorphous silicon with respect to crystalline silicon [46]. Amorphous silicon also pulverizes less than crystalline silicon. The crystalline silicon core directly addresses the detachment issue by forming a strong mechanical support and electron transportation path for the nanowires. The shortcoming of this type of nanowire is that it requires the cutoff voltage to remain above 150 mV to prevent the entire nanowire from interacting with
Figure 1. Silicon nanowires before lithiation (top) and after lithiation (bottom) [28]. Scales of two SEMs are identical.
lithium and undergoing a crystalline to amorphous transformation in the core. This would lead to fatigue, large capacity fade, and risk breakage of the nanowires from the substrate. With a 0.2C current density and a 150 mV cutoff, a 960 mAh/g reversible capacity was possible after 100 cycles with 85% capacity retention. Most of the loss occurred on the first cycle when the efficiency was 80.4%. If the cutoff was changed to 10 mV, the reversible capacity increased to 2,000 mAh/g after 30 cycles, but the efficiency was only 79%. Since there is still some loss of capacity, breakage of the nanowires may still be playing a part in the anode performance. Regardless of the method by which the silicon is attached to the substrate, it is reasonable to expect some detachment. The substrate must be fabricated from an electrochemically inert material. Therefore, it will not expand as the nanowires do when they alloy with lithium. This leads to a stress buildup at the nanowires’ base that will eventually cause cracks and detachment.

Germanium nanowires grown by the same vapor-liquid-solid method as the silicon nanowires [12,47], produced a first cycle reversible capacity of 1,141 mAh/g and a irreversible capacity of 1,826 mAh/g. Over the next 19 cycles, the discharge capacity remains stable at approximately 1,000 mAh/g when tested with a C/20 rate. When the rate is increased to 2C, the capacity drops to 600 mA/g. These nanowires were 50-100 nm in diameter, 20-50 microns long, and like the silicon nanowires, do not pulverize. Also like silicon nanowires, the germanium nanowires do not retain their original shape when cycled. There is a considerable capacity loss which, again like silicon, may be attributed to breakage of the nanotubes and failure of lithium to de-alloy with the
germanium. Despite its lower intercalation, germanium has a potential advantage over silicon in that the room temperature diffusivity of lithium in Ge is 400 times higher than that in silicon, possibly making it a better material for high power rate applications [1]. While germanium does not expand as much as silicon when alloying with lithium, there will still be stresses at the nanowires’ base. As with the silicon nanowires, the concentrated stress leads to cracking and detachment of the germanium nanowires.

In a novel application of SnO$_2$ for anodes, nanowires were grown on stainless steel by the thermal evaporation technique and vapor-phase transport synthetic method [3]. These nanowires were electrochemically tested over a 0.00 to 1.2 volt range at multiple rates to determine its performance. At 1C, the total capacity of the SnO$_2$ was 2,140 mAh/g after the first cycle, but the reversible capacity was 800 mAh/g. After 50 cycles, the reversible capacity dropped to 510 mAh/g. As the charge/discharge rate was increased, there was a corresponding decrease in the specific capacity. For example, at 3C the reversible capacity falls to 530 mAh/g after 20 cycles. At 10C the reversible capacity was 440 mAh/g after 40 cycles.

The volume expansion of tin-oxide as it alloys with lithium is less than both silicon and germanium, but still 300% [3]. In bulk form, it naturally leads to pulverization of the material and drives the investigation of alternate methods of using tin-oxide, such as nanowires. However, like the silicon and germanium nanowires, the substrate must be an inert, conductive material such as stainless steel or copper. If the substrate does not expand as the tin-oxide does when it alloys with lithium, there will be stresses at the base of the nanowires that will eventually lead to breakage.
Still, it has been demonstrated that the both carbons and metalloids have attractive properties for anodes. Therefore, the logical extension of anode material development is the study of composite materials that will be expected to exhibit the best qualities of the carbons and metalloids.

2.2.3. Nanocomposites

To combine the best qualities of carbon and silicon, some researchers have examined the feasibility of silicon/carbon (Si/C) composites as anode materials. These materials have been prepared by decomposition of organic precursors, using high-energy mechanical milling, or a combination of both (Figure 2) [4].

Nanocomposites have been fabricated with pyrolyzed, mechanically milled silicon and polystyrene resin or by moderate ball milling of carbon (graphite, disordered carbon, meso carbon microbeads, etc.) and nanocrystalline silicon. The silicon nanoparticles alloy with lithium without pulverizing while the polystyrene resin forms a matrix that accommodates the silicon’s expansion. Most of the capacity loss occurs when the silicon de-alloys from the lithium and shrinks. As it shrinks, there is a loss of electrical contact with the matrix around it. Therefore, it is necessary for the matrix to have a high mechanical strength to withstand the volume change of the silicon [39], or be elastic enough to shrink when the silicon shrinks.

At a rate of 100 $\mu$A/cm$^2$, the pyrolyzed silicon and polystyrene resin nanocomposite has a reversible capacity of 850 mAh/g with a 1.1% loss of capacity each cycle [48]. The primary cause of capacity loss was from the inability of the matrix to resist the
expansion of the silicon. This caused a loss of electrical contact between the silicon nanoparticles and the matrix as the silicon de-alloyed from the lithium and shrank.

The ball-milled carbon and nanocrystalline silicon achieved a first cycle total capacity of 800-1,400 mAh/g, but with poor capacity retention [49-51]. The poor capacity retention of Si/C nanocomposites may arise from incomplete dispersal of silicon throughout the carbon matrix, and longer milling times may be needed to create better adhesion between the silicon and carbon [49]. However there is a limit to how much milling is allowable. Excessive milling, approaching or exceeding five hours causes the formation of silicon-carbide (SiC) [52,53]. As the milling time increases, the weight fraction of SiC increases while the weight fraction of silicon decreases, and after 15 hours, the silicon phase is almost completely consumed [54]. This SiC phase is electrochemically inactive and does not contribute to the capacity of the anode [4,48].

To prevent the formation of SiC and reduce the amorphization of graphite, which also takes place in long milling operations, polyacrylonitrile has been used as a diffusion barrier and o-cresol novolac epoxy resin has been used to bypass SiC formation during 15 hour milling operations [4,54]. These nanocomposites demonstrated reversible capacities of 660 and 640 mAh/g, respectively, at 160 mA/g, and there is almost no capacity fade after 25-30 cycles.

Comparing the electrochemical performance of ball-milled silicon/carbon nanocomposites, it has been demonstrated that the silicon nanoparticles size is very important to anode efficiency [55]. The nanocomposites in question were made with ball-milled silicon particles (less than 1 micron in size) and nanosized silicon powder (30-
Figure 2. SEM images of a silicon/carbon ball-milled nanocomposite before (top) and after (bottom) 30 cycles [42].
50 nm), each blended with graphite and pitch to form anodes. The expected outcome was that higher percentages of silicon led to higher reversible capacities and higher first cycle capacities. However they also generated higher irreversible capacities and lower first cycle efficiencies. Most importantly, the nano-sized particles performed better than the near-micron-sized particles with a 27 percent higher first cycle capacity and 7 percent higher first cycle efficiency. This clearly indicates the utility of nano-sized particles in Si/C anodes.

A method to incorporate silicon nanoparticles into a nanocomposite is to encapsulate the silicon with a layer of carbon (Figure 3) [5]. This was accomplished by first treating the silicon with silylating reagent to render them hydrophobic, allowing the silicon nanoparticles to be covered with a resorcinol-formaldehyde microemulsion. Carbonization of the nanoparticles was the final step. When electrochemical testing was performed, there was irreversible capacity loss on each cycle. On the first cycle at a 50 mA/g rate, the total capacity was 1,730 mAh/g while the reversible capacity was 930 mAh/g. Three causes for the capacity loss were proposed: 1) solid electrolyte interphase (SEI) formation on the carbon surface, 2) Li$^+$ trapping in voids or cavities in the carbon, and 3) Li$^+$ trapping in the silicon matrix. Another mechanism for capacity loss is that as the silicon nanoparticles de-alloy from the lithium, they shrink within the carbon coatings (which expanded when the silicon expanded with lithium). The silicon nanoparticles inevitably begin to lose electrical contact with the carbon.

While silicon can be successfully coated with carbon, it can also be used to coat CNFs. A nanocomposite of CNFs and carbon fibers coated with silicon was capable of storing
Figure 3. SEM (top) and TEM images of carbon-coated silicon nanoparticles prepared via an R-F microemulsion [51].
766 mAh/g after 20 cycles at a 50 mA/g rate [56]. Vital to the function of this material was that as the silicon coatings distorted from repeated expansion and shrinking, it remained in contact with its CNF supports. This behavior was possible because the silicon coating was concentric with the CNF under it and was unable to separate from the CNF.

Another material that is frequently considered for a nanocomposite is tin. Tin has a fairly high theoretical specific capacity (981 mAh/g for Sn and 1,491 mAh/g for SnO₂) [2]. Like silicon, tin has a low reduction potential versus CNTs (+0.5V for CNT, -0.09V for SnO₂, and +0.15V for Sn⁴⁺). Therefore, electrodeposition of these metals onto CNTs is problematic. However, methods have been developed for attaching tin nanoparticles onto CNTs with functional groups [2,6]. This has not yet been accomplished for silicon. Tin has also been combined with antimony for coating carbonaceous materials in anodes.

A tin-antimony (SnSb) alloy which has been depositied on the surface of mesophase carbon microbeads (MCMB) by co-precipitation in glycerin solution [57] rendered performance that varied with the amount of SnSb coating the MCMBs. The best performance was obtained with a 30% weight percentage of SnSb was used. This formulation yielded its highest capacity after 25 cycles (380 mAh/g) and the lowest overall irreversible capacity (110 mAh/g). While higher concentrations of SnSb initially surrendered higher capacities, their performance quickly dropped off because they were more susceptible to agglomeration of the nanoparticles. When nanoparticles such as SnSb or silicon are smaller than 100 nm, they aggregate more aggressively as lithium
is inserted and extracted [57,58]. With lower concentration of SnSb, the agglomeration is more likely to occur at sites where MCMBs meet, bringing the SnSb nanoparticles into close proximity with each other. If the nanoparticles are bound into place, higher concentrations may be used without risk of agglomeration.

Acidic solutions may be used to functionalize CNTs and attach SnO$_2$ nanoparticles to them (Figure 4), but results in an anode with high fade and irreversible capacity after 20 cycles [6]. The second cycle reversible capacity of this type of material can attain 810 mAh/g at 0.1C while the irreversible capacity was 710 mAh/g. The capacity continues to fall off to 404 mAh/g after 20 cycles. Possible causes of the high irreversible capacity are detachment of the nanoparticles from the CNTs and the formation of the SEI layer over the CNTs. In a material like this, the SEI layer can isolate the more conductive CNTs and drive up the loss [59].

A material that may have effectively maintained good contact between the CNTs after the SEI was formed consisted of CNT sheets of aligned tubes [2]. The CNT sheets were also coated with SnO$_2$ nanoparticles (Figure 5). The sheets were functionalized with poly(vinylpyrrolidone) (PVP), which captured the SnO$_2$ nanoparticles. This resulted in an anode material with very stable performance, up to 950 mAh/g (reversible capacity) at 0.1C over 70 cycles. Another aid to the high reversible capacity that the material was tested as single sheets, eliminating the additional loss of conductivity that occurs as anode materials become thicker. As we saw in graphene anodes, the best performance is obtained when the anode thickness is minimized.
Figure 4. SEM image of SnO₂ nanoparticles deposited onto CNTs [52].

Figure 5. SEM image of Aligned and SiO₂ coated CNTs for a Li-ion battery anode[5].
Depositing uniform tin coatings onto CNTs avoids the complications caused by the expansion of tin as it alloys with lithium. Also, placing the tin in direct contact with the CNTs allows the CNTs to be used as current carriers. Despite the promising results, tin’s capacity is greatly exceeded by silicon’s and there is far more to be gained by creating a silicon/carbon nanocomposite.

2.2.4. Intercalation and Alloying

Understanding lithium intercalation is essential regardless of the anode material being considered. However, due to the obvious differences in structure between SWNTs, MWNTs, and metals, lithium uptake will take place in different ways.

Depending on the fabrication method and additional processing, CNTs may be open or closed ended. The interior of closed CNTs is not accessible to lithium. Therefore, another mechanism is necessary for intercalation. Matsumura et al. [60] proposed that lithium is intercalated between graphene sheets, doped at graphene layer edges, and doped onto the surface of layers. If the CNT caps are removed, some believe that lithium may be intercalated in the interior of the tubes [21,27]. However, it is also suspected that lithium intercalated in to the interior of tubes cannot be removed and contributes to the irreversible capacity.

Most of the loss of reversible capacity in carbon anodes takes place after the first lithiation, and part of this irreversible capacity is attributed to the formation of the SEI [61-63] on the surface of the anode. Additional processing of the CNTs, such as ball-milling, increases capacity by fracturing the tubes and creating defects for lithium
intercalation. Again, the lithium is not easily de-intercalated from these defect sites, and the irreversible capacity is much higher than in raw CNTs.

In the case of nanowires, lithium alloys into the sides and causes a noticeable change in the nanowire profile (Figure 1), expanding its volume by 400% for silicon, 370% for germanium, and 300% for tin-oxide [1,3]. As discussed previously, in nanowires the SEI is not the only cause of capacity loss and breakage of the nanowires is suspected.

Silicon atoms can alloy with a maximum of 4.4 lithium atoms, yielding a Li_{22}Si_{5} alloy when its theoretical specific capacity of 4,200 mAh/g is attained [38,64,65]. At this point, the Li-Si unit cell is at its maximum volume (659.2 cubic angstroms). As the lithium de-alloys, the volume quickly drops. Since the original volume of the silicon atom is 160 cubic angstroms [38], it is very difficult for the lithiated silicon atoms to maintain contact with a surrounding matrix as it shrinks. Therefore as the electrical contact becomes less robust, less lithium can be removed from the anode. Even germanium and tin-oxide, with lower levels of expansion as they alloy with lithium than silicon, are faced with an identical problem. Germanium forms a Li_{22}Ge_{5} alloy when saturated with lithium and has a theoretical capacity of 1,625 mAh/g [36].

The alloying process for tin-oxide has been proposed to be more complex [66]. It is a two-stage process where lithium first binds to the oxygen atoms to form 2Li_{2}. This reaction is not reversible. The tin reacts with lithium to form Li_{x}Sn, which in its fully lithiated form is a Li_{4.4}Sn alloy with a theoretical capacity of 994 mAh/g [67].

To compensate for irreversible losses, Li-ion cells are normally made with excess cathode material, and this increases the overall cost of the battery [68]. For this and
other reasons, improvements to the anode must be matched by improvements to the cathode to more completely address performance issues in the batteries.

2.3. Cathodes

2.3.1. Current Cathode Materials

Equally important as the anode, but not receiving as much attention, is the cathode. Since Sony’s introduction of its Li-ion batteries, lithium cobalt oxide (LiCoO$_2$) has been the cathode material of choice because of its high lithium mobility and high electrochemical potential versus lithium (approx. 4 V), although its capacity is only 140 mA h g$^{-1}$ [10]. It has also proven itself to be reliable and has a long cycle life. This material has its detractors because of the high cost and the toxicity of cobalt. LiCoO$_2$ cathodes account for approximately 41% of the total battery cost [69,70].

Perhaps more important than cost, the safety performance (and image) of Li-ion batteries must be improved. After the very publicized laptop battery fires of 2006, it was believed that exothermic reactions between the cathode material and liquid electrolytes were the cause of the failures [71]. As this reaction takes place, lithium deposited on the anode accelerates the reaction and causes a spike in temperature [72-74]. This in turn changes LiCoO$_2$ into Co$_2$O$_3$, an oxidizing agent that releases oxygen [75]. Probably more than anything, safety issues loom over the success of Li-ion batteries.

Some cathode compositions being explored are lithium cobalt nickel oxide (LiCo$_{0.2}$Ni$_{0.8}$O$_2$), and lithium manganese oxide spinel (LiMn$_2$O$_4$). The polyanion compounds (Li$_x$M$_y$(XO)$_z$, M = transition metal; X = P, S, As, Mo, or W) provide another
class of cathode materials for Li-ion batteries [76]. Of these polyanions, lithium iron phosphate (LiFePO4), has attracted much interest. Some of these materials only address performance and cost improvements, while other also address safety.

2.3.2. LiCoO2 Modifications

In the sole interest of safety improvement, LiCoO2 cathodes were coated with aluminum phosphate (AlPO4) nanoparticles by depositing them directly from an aqueous solution [75]. This was a nanoscalar coating 15 nm thick. These cathode were compared to conventional cathodes in overcharge safety tests which dictate that even though the battery cells may swell, they may not explode or catch fire [34,77]. Each of the uncoated cathode cells fell into thermal runaway and burned, the coated cathode cells did not. This is because the P-O bonds in the coating are very resistant to chemical attack [34,78,79], more so than LiCoO2. A possible additional benefit of the AlPO4 coating is increased capacity retention. After 20 cycles, the coated cathodes showed only a 1% loss of capacity, compared to a 12% loss in bare LiCoO2 [75].

Likewise, cyanoethyl polyvinylalcohol (cPVA) encapsulated LiCoO2 cathodes displayed resistance to thermal runaway and did not burn in 160°C oven tests [71,80], while conventional LiCoO2 cathodes maintained their well-known behavior and burned [34,81]. The cathodes were coated by dipping them into a cPVA solution (with acetone as a solvent) for 10 minutes. The cPVA coated cathode cells did not show any change in electrochemical performance and capacity compared to conventional LiCoO2 over 350 cycles.

2.3.3. LiCo0.2Ni0.8O2
With the substitution of a portion of the cobalt with nickel in the traditional LiCoO$_2$ cathode, LiCo$_{0.2}$Ni$_{0.8}$O$_2$ can provide an improvement in capacity (180 mA h g$^{-1}$) with lower cost than LiCoO$_2$ [82]. However, it still has toxicity issues and is relatively expensive. This material has also been unstable when overcharged and loses power quickly when aged as the cell impedance increases [83]. Over a month of aging at 50°C, the area specific impedance (ASI) of these anodes increases from 30 to 240 Ω cm$^2$. Over the same time period, aluminum doped LiCo$_{0.2}$Ni$_{0.8}$O$_2$’s ASI is almost unchanged. Doping LiCo$_{0.2}$Ni$_{0.8}$O$_2$ with no more than 5% aluminum along with managing the powder morphology to minimize the cathode surface area size increased the cell’s impedance stability and capacity retention [83]. Doping with 10% or more Al results in capacity losses that increase as the Al content is increased [84]. This material is now frequently used in commercial battery cells. Small gains can be made by modifications to LiCoO$_2$, but to make the leap customers demand, other cathode compounds must be studied.

2.3.4. LiMn$_2$O$_4$

Lithium manganese oxide (LiMn$_2$O$_4$) [85-87] is a good alternative to LiCoO$_2$ and found use in large industrial applications. It costs less, is less toxic, and has good thermal stability and safety. However this material has shown limitations in cycle life, storage instability, and a capacity less than LiCoO$_2$ (110 mA h g$^{-1}$) [69,82]. Multiple efforts indicate that improvements can be made to certain properties of LiMn$_2$O$_4$.

To address cyclability issues, H.S. Moon et al. [88] substituted Co ions for a portion of the Mn ions in order to improve the structural and electrochemical properties in a thin film form. In this case, LiMn$_2$O$_4$ had a better first discharge capacity than
LiCo$_{0.26}$Mn$_{1.74}$O$_4$ (40 $\mu$Ah/cm$^2$-\(\mu\)m versus 34 $\mu$Ah/cm$^2$-\(\mu\)m). However, the LiMn$_2$O$_4$ capacity continually diminished with each successive cycle, dropping to 23 $\mu$Ah/cm$^2$-\(\mu\)m after 50 cycles at a current density of 100 mA/cm$^2$. The LiCo$_{0.26}$Mn$_{1.74}$O$_4$ capacity dropped only slightly to 32 $\mu$Ah/cm$^2$-\(\mu\)m over the same number of cycles [88].

To address capacity fade after high temperature storage, Park et al. coated LiMn$_2$O$_4$ with fine LiNi$_{1-x}$Co$_x$O$_2$ (X = 0.2 and 1) particles [89]. The cathode’s high temperature fade problem is believed to be associated with Mn$^{2+}$ dissolution induced by HF acid produced by secondary reactions in the electrolyte as it decomposes [90]. This coating suppresses electrolyte decomposition, reduces Mn dissolution and allowed no capacity loss of the cathode after 300 hours of storage at 65°C [89]. These efforts did not sufficiently impact the capacity of LiMn$_2$O$_4$.

An alternate method of reducing capacity fade in LiMn$_2$O$_4$ spinel is to change the electrolyte. Amine et al. [91] documented that the use of lithium bis(oxalato)borate (LiBoB) as an electrolyte salt in place of LiPF$_6$ significantly decreased the amount of fade in LiMn$_2$O$_4$ battery cells. Over 100 cycles, spinel in LiPF$_6$ electrolyte faded 50% at 55°C while fading 20% in LiBoB. This occurs because LiBoB does not produce a strong acidic environment that can contribute to Mn$^{2+}$ dissolution.

### 2.3.5 Olivines

Lithium metal phosphates (olivines) have shown the potential to overcome many deficiencies in current cathodes. The major benefits of using olivines are greater abuse tolerance and increased capacity. The abuse tolerance trait arises from the covalent bonds of PO$_4^{3-}$ [81,92]. However, these same bonds reduce the conductivity of the
olivines. Four olivines of interest are LiFePO$_4$, LiMnPO$_4$, LiNiPO$_4$, and LiCoPO$_4$. LiNiPO$_4$ and LiCoPO$_4$ are being developed for future use and are incompatible with current electrolytes because of their high charge voltages of 5.1V and 4.8V, respectively. Their attractiveness comes from their competitiveness with LiCoO$_2$ and LiAl$_{0.05}$Co$_{0.15}$Ni$_{0.8}$O$_2$ in energy density. LiMnPO$_4$ does not seem to be garnering much interest at this moment. The most likely reason for this may be because LiMnPO$_4$ is classified as an insulator, not a quality being sought in cathode materials [93]. This material also undergoes Jahn-Teller distortion when delitiated [94], causing the conductivity to drop and the capacity to rapidly fade when cycled. However changing to a material such as LiMnPO$_4$ reduces the cathode cost percentage to approximately 11%, compared to LiCoO$_2$, which accounts for 41% of battery cost [69].

2.3.6 LiFePO$_4$

LiFePO$_4$, on the other hand, is gaining commercial acceptance despite being classified as a semiconductor. It offers a specific capacity of 170 mA h g$^{-1}$ while costing approximately 62% less than LiCoO$_2$ [69]. Safety-wise, it is non-toxic, and has the benefit of the strong covalent bonds that make it more stable in an overcharging situation [76,95]. Like the AlPO$_4$ coating for LiCoO$_2$ cathodes, LiFePO$_4$ is very resistant to chemical attack. However, it falls short of LiCoO$_2$ in its rate capability due to low electronic conductivity ($10^{-9}$ to $10^{-10}$ S cm$^{-1}$ [96-99]), and is therefore not ideal for high power applications. LiCoO$_2$’s electronic conductivity is $7.25\times10^{-5}$ S cm$^{-1}$ (also a semiconductor) [100]. This property has held back widespread use.
LiFePO$_4$’s primary deficiency has been experimentally overcome by carbon coating the cathode material. Chen et al. [101] used a multiple step, high temperature method to fabricate a LiFePO$_4$/C composite material. NH$_4$H$_2$PO$_4$, CH$_3$COOLi, and FeC$_2$O$_4$.2H$_2$O were pressed into pellets and heated at 350°C in nitrogen gas for 6 hours. They were then cooled, ground, mixed with 6wt% guluronic acid, and heated at 700°C for 10 hours. The LiFePO$_4$/C samples exhibited an electrical resistance of 0.67mΩ versus 43KΩ for conventional LiFePO$_4$. At a 0.2C rate the LiFePO$_4$/C’s specific capacity was 140 mA h g$^{-1}$ while the uncoated LiFePO$_4$’s was 115 mA h g$^{-1}$. At a 1C rate the uncoated cathode’s capacity dropped to 10 mA h g$^{-1}$.

In a similar experiment, Shin et al. fabricated and tested carbon coated LiFePO$_4$ cathodes to improve its conductivity [102]. Coated and uncoated electrodes were made side by side using similar starting materials, except 5 wt.% acetylene black powders were added to the coated cathodes’ starting materials. LiCO$_3$, FeC$_2$O$_4$.2H$_2$O, and NH$_4$H$_2$PO$_4$ were mechanochemically activated in a planetary mill with zirconia balls for three hours. These powders were heated to 700°C in an Ar+5% H$_2$ atmosphere for 10 hours. The carbon coated LiFePO$_4$ maintained a capacity of approximately 150 mA h g$^{-1}$ at 0.05C and 135 mA h g$^{-1}$ at 1C. After 30 cycles, the coated LiFePO$_4$ had an ohmic resistance (total resistance of the electrolyte, separator, and electrical contacts) of 4.479 ohms, compared to the uncoated LiFePO$_4$’s resistance of 22.09 ohms.

A. Yamada et al. [94] reported achieving 165 mA h g$^{-1}$ in LiFePO$_4$ when the particle size was decreased and sintering temperatures were between 500-600°C. Hindrances to
optimizing performance were particle growth when temperatures exceeded 600°C and non-crystalline Fe$^{3+}$ when the temperature was less than 500°C.

As discussed previously, the methods to fabricate coated LiFePO$_4$ required heating of the cathode powders for several hours in controlled atmospheres. Murugan et al. [103] have taken note of this and developed a novel process that does not require controlled atmospheres and reduces the fabrication time of coated LiFePO$_4$ particles. These particles are not coated with carbon, but with a conducting polymer. In this process, lithium hydroxide and iron (II) acetate are dissolved in tetraethyleneglycol. After phosphoric acid was added, the mixture was heated in a microwave synthesis system at a power of 600W, raising the temperature to 300°C for five minutes and forming LiFePO$_4$ nanoparticles. The nanoparticles were mixed into a p-toluene sulfonic acid doped poly (3,4-ethylenedioxythiophene) [104] and ethanol colloidal solution and coated. The coated nanocrystals were then dried. Once formed into cathodes, the nanocrystals achieved a discharge capacity of 166 mA h g$^{-1}$ with 3% fade over 50 cycles.
3. CHARACTERIZATION TECHNIQUES

Several characterization techniques used in this research. These mostly involved microscopes and are discussed in this chapter.

3.1. Scanning Electron Microscope (SEM) Characterization

SEM characterization is similar to optical microscopy, except uses electrons instead of light to create images of the surfaces of materials. A FEI Sirion field emission SEM (FESEM) was used for surface characterization of the samples before and after electrochemical cycling. This device was used to magnify images up to 250,000 times to study the dispersion of the anode constituents and the formation of deposits on the anode surface and constituents after electrochemical tests. The accelerating voltage was varied from 5 to 20 kilo-electron-volts (keV), depending on how charges built up on the materials. In some cases the material was cut and SEM images were taken of the interior of material. The Sirion SEM had no capabilities to perform elemental analysis.

3.2. Transmission Electron Microscope (TEM) Characterization

A FEI Titan TEM and a Phillips CM200 Lab 6 TEM were used for characterization of sample components. These components included individual CNTs, CNFs, and silicon and tin-oxide nanoparticles. These devices were used to magnify images up to 300,000 times with an accelerating voltage of 200 kilovolts (kV) and could observe the condition of CNTs and CNFs following electrochemical tests. While both TEMs are capable of elemental analysis, the Titan TEM can also create images which highlight the elements.
3.3. X-Ray Diffraction

In X-ray diffraction, a target (usually copper) is bombarded by electrons, which have been accelerated by a cathode ray tube filament. The accelerated electrons dislodge electrons in the target from their shells, producing X-ray spectra. The X-rays are filtered to make them monochromatic and directed to the sample to be characterized. The sample is rotated as the intensity of the reflected X-rays is recorded. The technique is often used to characterize crystalline materials, or identify unknown crystalline materials. X-ray diffraction was used in this work to look for changes in the structure of CNTs and CNFs and to identify compounds found in the cycled anode materials.

3.4. Raman Spectroscopy

In Raman spectroscopy, electrons in the material to be studied are excited by photons from a laser. The electrons move to the conduction bands, release photons and return to the valence bands. The wavelengths of the emitted photons are different from that of the exciting laser. These emissions are collected and displayed as a spectrum with identifiable peaks. The wavelengths of the peaks can be used to identify constituents of the material being analyzed or characteristics of the material. Raman spectra were obtained with a Renishaw inVia microscope and a neodymium-yttrium-aluminum-garnet laser operating at 532nm.
4. TEST METHODS

4.1. Electrochemical Testing

This research relied upon the fabrication of anode materials that were electrochemically tested to determine their charge/discharge characteristics, specific capacity, and short-term performance. Well in excess of one hundred electrochemical studies were performed on baseline materials and candidate materials. These were accompanied by characterizations of the materials before and after the electrochemical tests to understand the mechanisms affecting the performance of the materials.

A test matrix of candidate materials was assembled. This matrix was based on varying concentrations of the base materials used in the anode fabrication. While not all samples in the matrix were fabricated and tested due to time restrictions, all the samples were processed in a similar manner. Prior to the execution of the test matrix, an understanding of the performance characteristics of the base materials was created by performing electrochemical tests of these materials. For each electrochemical test, data sets that include charge and discharge curves and specific capacities cycle were created.

A Maccor 4300 battery testing system is at the center of the electrochemical testing. This device can simultaneously test up to eight battery cells through a programmable controller. Each test program can vary the charge and discharge rates, the number of cycles, and the upper and lower voltage limits. In Table 1, a number of test profiles used in this effort are given. Profile number 1 is used to determine the best charge rate for
the material in question. If the capacity does not drop off as the charge/discharge rate is increased, this indicates that the material is capable of fully intercalating lithium ions at the higher rate. Profiles 2 and 3 are for constant rate tests and can be used to gather data on a material’s long term performance. A charge/discharge rate of 50 mA/g is most often used as it provides a good balance between material capacity and test duration. An electrochemical test of a material with a high specific capacity can last several weeks until the electrolyte is exhausted.

Electrochemical testing was performed in an argon-filled glove box by mounting the anode samples onto copper or stainless steel electrodes, layered with a Celgard 2500 membrane soaked in electrolyte, and a lithium foil disk (Aldrich) (Figure 6). The electrolyte used was 1M LiBF₄ in a 1:1 mixture of DEC and EC.

Half-cells with silicon were cycled from 0.02V to 2V at a predetermined charge/discharge rate with the Maccor 4300 battery testing system, while all other samples were cycled from 0.02V to 3V. Unless the electrodes were recently removed from an oven, they were heated on a hot plate in the glove box with an argon atmosphere for 1 hour at 250°C to ensure any absorbed moisture was removed prior to electrochemical testing.

The electrochemical tests were used to analyze the anode materials’ performance. These data include charge and discharge capacities and voltages, specific capacities with each cycle, energy, and temperature. These data are normally presented in graphical form. The first cycle charge and discharge curves, and the capacity versus cycle curve.
are most often used in anode performance analysis. The first cycle discharge curve is useful in understanding the SEI formation on the anode and lithium intercalation into the anode. When the anode specific capacity is observed over several cycles, an indication of the material’s stability can be derived. While there is normally a drop in capacity between the first and second cycles, capacity losses in successive cycles is often caused by break downs in the internal structure of the anode.

<table>
<thead>
<tr>
<th>Profile</th>
<th>Discharge Current (mA/g)</th>
<th>Charge Current (mA/g)</th>
<th>Number of Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
<td>20</td>
</tr>
</tbody>
</table>
Figure 6. Diagram of electrochemical testing setup.
4.2 Empirical Evaluation

With the anode fabrication methods and testing methods developed in the baseline studies, the test anodes could be fabricated and evaluated. The metrics of importance were the total capacity, the reversible capacity, and the irreversible capacity. These properties can be used to quickly identify anodes that are suitable for further evaluation or to determine if improvements are required. To obtain these performance figures, the anodes are tested in similar conditions. Physical characterization of the anodes was also performed in order to understand the mechanisms underlying the observed performance.

4.3. Experimental Design and Procedure

In designing the experiment for this research, it was necessary to observe and substantiate the benefits of one type of CNT over another and the performance advantage, if any, gained by using CNFs in the anode composition. This would aid in testing some of the hypotheses presented in Chapter 1. Several compositions of anode materials were considered for this effort (Table 2), but not all were fabricated or tested. The theoretical capacities of these anodes are shown in Table 3. Tin-oxide based anodes were fabricated first because the use of an inert atmosphere to protect them from oxygen was not necessary. This would be required for the silicon based anodes. Varying the tin-oxide or silicon content was of interest in order to get an indication of the maximum amount that the anodes could function with.
Ideally, the silicon or tin-oxide content in the anode must be maximized for the best capacity. For this reason, two content levels were considered in this test series to produce some information on how the performance changes with the silicon or tin-oxide content. It is expected that if the metal content is too high, the nanoparticles may be placed in physical contact with each other and agglomerate and irreversibly trap lithium.

4.4. Anode Fabrication

The anodes were fabricated into buckypapers by filtration via negative pressure using the following procedure: Mixtures of CNTs (SES Research), CNFs (ASI PR-25-XT-PS), and silicon or tin-oxide nanoparticles (Aldrich) were dispersed in 100ml of n-methylpyrrolidone (NMP) (Burdick and Jackson) in a Branson 3510 bath sonicator for three hours or with a 600 watt ultra-sonicator (Sonics & Materials, Inc GEX600-5) set at either 20 or 40% amplitude for 10 to 60 minutes. A 42mm cellulose filter (Whatman 1006 042) was placed in a Buchner funnel and moistened with NMP. A vacuum was applied to the funnel with a Buchner flask to aid the filtering of the mixture as it was slowly poured into the funnel. The resulting paper was dried in a vacuum furnace at 10mbar and 125°C for 24 hours to remove the NMP. The buckypaper could then be peeled from the surface of the filter cut into small pieces for electrochemical testing. Photographs of the anodes are shown in Figure 7.

Later iterations of the anode material were infiltrated with a phenolic resin (Durite SC-1008, Hexion Chemicals) or sonicated in acetone containing a percentage of phenolic
Table 2 – Anode Compositions

<table>
<thead>
<tr>
<th>Anode</th>
<th>SnO₂%</th>
<th>Si%</th>
<th>SWNT %</th>
<th>MWNT %</th>
<th>CNF %</th>
<th>Tested?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition A</td>
<td>75</td>
<td>20</td>
<td>5</td>
<td>Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition B</td>
<td>75</td>
<td>20</td>
<td>5</td>
<td>Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition C</td>
<td>70</td>
<td>24</td>
<td>6</td>
<td>Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition D</td>
<td>50</td>
<td>40</td>
<td>10</td>
<td>Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition E</td>
<td>50</td>
<td>40</td>
<td>10</td>
<td>Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition F</td>
<td>50</td>
<td>50</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition G</td>
<td>50</td>
<td>50</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition H</td>
<td></td>
<td>75</td>
<td>20</td>
<td>5</td>
<td>N</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 – Theoretical Capacities of Anode Compositions (mAh/g), 1ˢᵗ Cycle/2ⁿᵈ Cycle

<table>
<thead>
<tr>
<th>Anode</th>
<th>SnO₂ %</th>
<th>Si%</th>
<th>SWNT %</th>
<th>MWNT %</th>
<th>CNF %</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition A</td>
<td>1,118.3/735.8</td>
<td>74.4</td>
<td>18.5</td>
<td>1,211.2/828.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition B</td>
<td>1,118.3/735.8</td>
<td>74.4</td>
<td>18.5</td>
<td>1,211.2/828.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition C</td>
<td>1,043.7/686.7</td>
<td>89.3</td>
<td>22.3</td>
<td>1155.3/798.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition D</td>
<td>745.5/490.5</td>
<td>148.8</td>
<td>37.2</td>
<td>931.5/676.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition E</td>
<td>745.5/490.5</td>
<td>148.8</td>
<td>37.2</td>
<td>931.5/676.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition F</td>
<td>745.5/490.5</td>
<td>186</td>
<td>Y</td>
<td>931.5/676.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition G</td>
<td>745.5/490.5</td>
<td>186</td>
<td>Y</td>
<td>931.5/676.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition H</td>
<td>3,150</td>
<td>74.4</td>
<td>18.5</td>
<td>3,242.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7. Photographs of 50% SnO$_2$ 40% SWNT 10% CNF (top), 50% SnO$_2$ 50% SWNT (middle), and 50% SnO$_2$ 50% MWNT (bottom) buckypapers.
The anodes containing resin were later carbonized. This was done in order to adhere the nanoparticles to the CNTs and CNFs. This modification was necessary when SEM images showed that the nanoparticles were not securely bound to the surface of the CNTs and CNFs and would not remain in place during electrochemical cycling. A second intended benefit of carbonization is hard connections may be made between the CNTs and CNFs, making the anode more robust under cycling.

Vacuum infiltration of the phenolic resin into the buckypaper was accomplished by applying a vacuum to the buckypapers and then pouring on the resin. When the vacuum was removed, the resin was drawn into the buckypaper. Prior to infiltration, the resin with thinned with acetone. This step was necessary to lower the resin’s viscosity and permit it to be infiltrated into the buckypapers. The buckypapers were in the thinned resin for three hours and then placed into an oven for curing. Both the anodes infiltrated with resin and sonicated in resin were cured in a Memmert vacuum oven which was programmed as follows:

- Ramp up to 93°C
- Hold at 93°C for 24 hours (removes acetone)
- Increase temperature to 177°C
- Hold at 177°C for 2 hours (cures resin)
- Cool to room temperature
After the resin had cured, the buckypaper was next placed into a tube furnace for carbonizing. The tube furnace temperature was ramped up to 1,000°C, held at that temperature for four hours, and allowed to cool. Carbonizing of the anodes is not expected to damage the CNTs and CNFs because the process takes place in an argon atmosphere.

4.5. Empirical Analysis

The resulting data from the electrochemical tests are compared to the known performance of other anode materials that include graphite or carbon/silicon nanocomposites being developed elsewhere. Measurements of interest are the first cycle discharge capacity, the irreversible capacity, and the reversible capacity. The first cycle discharge capacity relates directly to the total capacity of the anode and can be used with the charge capacities from cycles of interest to calculate the irreversible capacity. The reversible capacity will be observed over multiple cycles to determine the stability of the anode and infer its long term performance. The expectation is that the capacity will stabilize and remain at a high level over the life of the electrochemical test. Some loss of capacity is normal on the first cycle when the SEI layer is formed.

The first cycle discharge curve is useful for understanding how the anode is intercalating with lithium. For example, most carbonaceous materials with the notable exception of CNFs, normally exhibit a plateau in their first cycle discharge curves at 0.8V when the electrolyte is reduced and the SEI layer forms (Figure 8) [21]. The CNF and silicon based anodes have no pronounced plateaus, indicating the materials’ surfaces...
better able to accommodate a more developed SEI resulting in less reduction of the electrolyte [105]. Additionally, silicon displays a curve with a slight negative slope between 0.3V and 0.02V that indicated alloying of lithium with silicon (Figure 9) [106].

Successive charge and discharge curves provide a quick analysis of the performance stability of the anodes. It is desired that these curves should overlay each other, indicating no loss of capacity (high efficiency) between the cycles.

SEM and TEM images are useful for visually inspecting the integrity of the anode and observing any breakdowns in the structure. These characterization methods may be extended to the FIB for observation of the internal structure of the anodes before and after cycling. Energy dispersive x-ray analysis (EDS) may also be used to determine the chemical composition of the anodes after cycling.
Figure 8. First and second cycle discharge curve for SWNTs (13).

Figure 9. First, second, and third charge and discharge curves for silicon nanowires (101).
Baseline studies were performed to gather data on the performance characteristics of the components of the anode material, SWNTs, MWNTs, CNFs, and tin-oxide. The studies began with electrochemical tests of a MWNT paper fabricated by the National Composite Center (NCC). This material is the result of a Materials and Manufacturing Laboratory project to increase the producible size of MWNT buckypapers to widths up to six feet. The paper is very uniform in appearance and characteristics. The NCC paper was used to create a sustainable, reliable test method and accumulate comparative data for the successive tests. The buckypaper was 65.75 microns thick, with a density of 0.348 grams per cubic centimeter (g/cm$^3$), and a conductivity of 49.77 seimens per centimeter (S/cm). This material was electrochemically tested using Profiles 1, 2, and 3 (Table 5).

FESEM and TEM images (Figures 10 and 11) of the NCC MWNT paper showed that the MWNTs were approximately 20-40 nm in diameter and over 1 micron long before electrochemical testing. Raman spectrum analysis showed peaks at 2,693 cm$^{-1}$, 1,579 cm$^{-1}$, and 1,345 cm$^{-1}$ (Figure 12). The 1,345 cm$^{-1}$ peak is within the D-bands (1,100 cm$^{-1}$ to 1,500 cm$^{-1}$), which indicate disordered carbons. The 1,598 cm$^{-1}$ peak is near the typical G-band peak of graphite (1,580 cm$^{-1}$), indicating the presence of crystalline carbons. The profile of the peak also indicates that the CNTs are semiconductor type.
The 2,693 cm\(^{-1}\) peak is near the G’ peak, an overtone of the D mode. Finally, the presence of an RBM peak at 190 cm\(^{-1}\) is an indication that some SWNTs are present.

It demonstrated a maximum specific capacity of 151.47 mAh/g after 20 cycles at 50 mA/g (Figure 13). At this point, the MWNT’s performance seems to have stabilized and it may well be capable of operating for several more cycles. With a first cycle discharge capacity of 976.10 mAh/g, the irreversible capacity over the 20 cycles was 824.63 mAh/g. Overall the NCC MWNT buckypaper’s performance is comparable to the MWNT paper performance data published by B. Landi et al [33].

Figure 14 shows the discharge curves of the NCC MWNT paper for cycles 1 through 5. As often happens with carbonaceous anodes, there is a large plateau in the first cycle discharge curve, indicating the formation of the SEI passivation layer. For this material, the plateau exists at 0.8 volts. The formation of the SEI layer is a contributor to the irreversible capacity since it traps lithium ions in the anode. While the loss of capacity is not desired, the SEI layer also provides some protection of the anode from the electrolyte, slowing its degradation. The similarity of curves 2 through 5 coincides with the stabilization of the successive charge and discharge capacities. This type of behavior is desired.

Nevertheless, the performance of the NCC paper is far below the theoretical capacity of carbon. However, it must be kept in mind that commercial anodes are fabricated on metal substrates in order to hold the material in a robust form and maintain electrical contact with it [30]. Aside from the effects of the SEI formation, another contributor to
the loss of capacity is the isolation of portions of the anode after the formation of the SEI layer [59]. Lithium ions are also theorized to become trapped within the MWNTs and contribute to the irreversible capacity [27].

Because the NCC paper did not contain the actual MWNTs used in the anodes fabricated for the research, baseline tests were repeated with MWNTs that were purchased from SES Research (catalog # 900-1260). These MWNTs were fabricated into buckypapers and used in the study.

Figure 10. SEM image of the NCC MWNT buckypaper.
Figure 11. TEM image of a MWNT after separation from the NCC buckypaper by sonication.

Figure 12. Raman spectrum of NCC MWNT paper before electrochemical testing.
Figure 13. Charge and discharge capacities of the NCC MWNT buckypaper anode over 20 cycles at 50 mA/g.

Figure 14. Charge and discharge curves for NCC MWNT buckypaper at a 50 mA/g rate.
6. **SES RESEARCH MULTI-WALLED NANOTUBE BUCKYPAPER ANODES**

The SES Research MWNTs were 10 to 30 nm in diameter and 1-2 microns long. FESEM and TEM images (Figures 15 and 16) confirmed these characteristics. Raman spectrum analysis of the MWNTs showed peaks at 2,681 cm\(^{-1}\), 1,578 cm\(^{-1}\), and 1,351 cm\(^{-1}\) (Figure 17). The 1,351 cm\(^{-1}\) peak is within the D-bands (1,100 cm\(^{-1}\) to 1,500 cm\(^{-1}\)), which indicate disordered carbons. The 1,578 cm\(^{-1}\) peak is near the typical G-band peak of graphite (1,580 cm\(^{-1}\)), indicating the presence of crystalline carbons and its profile indicates that the CNTs are semiconductor type. The 2,681 cm\(^{-1}\) peak is near the G’ peak, an overtone of the D mode. The presence of an RBM peak near 119 cm\(^{-1}\) is an indication that some SWNTs are present.

Using the same procedures defined in chapter 4, they were fabricated in to buckypapers by ultrasonication at 40% amplitude for 10 minutes in NMP, filtered, dried and electrochemically tested at a 50 mAh/g rate. MWNTs were expected to perform a large role in the materials, providing support for the tin-oxide nanoparticles and forming the conductive matrix.

The best performance of the SES MWNT buckypapers, tested at a 50 mA/g rate was found to be considerably less than the performance of the NCC paper and completed 20 cycles with a reversible capacity of 108.34 mAh/g (Figure 18). This difference in performance may be a function of how the buckypapers are fabricated. The NCC paper is fabricated under well controlled conditions to form a uniform, reproducible product. However, the SES MWNT paper was made in-house under less controlled, optimized
conditions. The lower performance of the SES MWNT buckypaper was also reflected in the charge and discharge curves (Figure 19). While the first cycle curves of the two MWNT papers were mostly similar, the SES buckypaper had a larger irreversible capacity and capacity losses on each successive cycle.

The SES MWNT buckypaper and the NCC MWNT buckypaper had comparable first cycle discharge capacities, approximately 1,000 mAh/g. Their charge capacities were also comparable up to the eighth cycle, when the capacity of the SES MWNT buckypaper began to fall off. At this point, it is assumed that the anode is beginning to disintegrate. The SES buckypaper is much less physically robust than the NCC buckypaper and is more likely to break apart.

TEM images of the SES MWNTs after cycling revealed no change in their structure (Figure 20). The lithium ions apparently intercalate and de-intercalate without significantly altering the MWNTs. Likewise, the SEI layer was not seen on the MWNTs. However, finding the SEI layer optically is difficult because it is often destroyed when the sample is prepared for microscopy.

An XRD study was also performed on the MWNTs. No changes were noticed in the MWNT structure (Figure 21), but the presence of LiF, an SEI component, was indicated. The presence of LiF is evidence that SEI layers may have formed within the anode, on individual MWNTs, in addition to the surface of the anode. Formation of the SEI within the anode may contribute to electrical isolation of portions of the anode [59].
Subjectively, the NCC buckypaper is more structurally cohesive than the in-house made SES buckypaper. Sheets up to 11 inches square were provided by NCC for this research. These sheets could be handled without risk of large scale break-up of the material. On the other hand, the SES MWNT buckypaper was very fragile. The structural integrity of the NCC MWNT buckypaper may well be a contributor to its superior performance to the SES MWNT buckypaper.

Figure 15. SEM image of MWNTs purchased from SES Research.
Figure 16. TEM image of SES Research MWNTs before electrochemical testing.

Figure 17. Raman spectrum of SES Research MWNTs before and after electrochemical testing.
Figure 18. Charge and discharge capacities of buckypaper fabricated with SES MWNTs.

Figure 19. Cycle 1-5 charge and discharge curves for buckypaper fabricated with SES MWNTs.
Figure 20. TEM image of SES Research MWNTs after electrochemical cycling.

Figure 21. X-ray diffraction spectra of SES Research MWNTs before and after electrochemical testing.
Like the MWNTs, SWNTs were also expected to play an important part in the anode’s performance. These were also purchased from SES Research (catalog # 900-1351). The SWNTs were less than 2 nm in diameter and 1-5 microns long (Figures 22 and 23). SWNTs have a tendency to bundle together in parallel. This was seen in the SES SWNTs as well. They were formed into buckypapers by ultrasonication at 40% amplitude for 10 minutes in NMP, filtered, and electrochemically tested. Raman spectrum analysis of the SWNTs showed peaks at 2,660 cm\(^{-1}\), 1,576 cm\(^{-1}\), and 1,339 cm\(^{-1}\) (Figure 24). The 1,339 cm\(^{-1}\) peak is within the D bands (1,100 cm\(^{-1}\) to 1,500 cm\(^{-1}\)), which indicate disordered carbons. The presence of this peak may also be an indication of defects within the SWNTs. The 1,576 cm\(^{-1}\) peak is near the typical G-band peak of graphite (1,580 cm\(^{-1}\)), indicating the presence of crystalline carbons and its shape indicates that the SWNTs are semiconductor type. The 2,660 cm\(^{-1}\) peak is near the G’ peak, an overtone of the D mode. Given that these are SWNTs, the presence of an RBM peak near 122 cm\(^{-1}\) is expected.

The SWNTs were tested at 50 mA/g. However, these anodes were only capable of producing a maximum of 31.44 mAh/g (Figure 25). While there was capacity fade throughout the first nine cycles, the reversible capacity eventually stabilized. The first cycle discharge curve was unremarkable, but exhibited a broad plateau at 0.8 volts (Figure 26). This plateau spans over 400 mAh/g, much greater than both of the MWNT buckypapers’ plateaus, possibly an indication of more SEI layer formation due to the
higher surface area of the SWNTs. This may also be the reason for the large irreversible capacity observed with the SWNTs. Another indication that the SEI layer and isolation of anode portions may be responsible for the large irreversible capacity is that the anode’s charge capacity is very stable throughout the electrochemical tests, while the discharge capacity deteriorates between the first and second capacity.

The overall performance of the SES SWNT buckypaper was much lower than that of SWNT buckypapers tested by Landi and Ng [29,30]. However, it must be noted that Landi, in particular used electrolytes that improved the electrochemical performance of the anodes. Additionally, Ng remarks that after 100 cycles the buckypaper was still intact, except for some small cracks. That was not the case with the SES MWNT buckypapers, which were very brittle and broke into smaller sections during electrochemical testing. Structurally, there was no apparent change in the SWNTs themselves as seen in Figure 27. However, the presence of LiF, a component of the SEI layer was noticed among the SWNTs when an XRD study was performed (Figure 28). This indicates that the SEI layer may have formed within the anode, possibly on the SWNT bundles and caused electrical separation of anode sections.
Figure 22. SEM image of a SWNT buckypaper anode.

Figure 23. TEM image of SWNTs purchased from SES Research before electrochemical testing.
Figure 24. Raman spectrum of SES Research SWNTs before and after electrochemical testing.

Figure 25. Charge and discharge capacities of buckypaper fabricated with SES SWNTs.
Figure 26. Cycles 1-5 charge and discharge curves for buckypaper fabricated with SES SWNTs.

Figure 27. TEM image of SES Research SWNTs after electrochemical cycling.
Figure 28. X-ray diffraction spectra of SES Research SWNTs before and after electrochemical testing.
8. APPLIED SCIENCES INC. CARBON NANOFIBER PAPER ANODES

Between five to ten percent of the material in the anodes would be CNFs, therefore knowledge of their baseline performance was required. CNFs (ASI PR-25-XT-PS) were fabricated into papers by dispersing them for three hours in NMP using an IKA Turrax shear mixer. After filtering and drying, the CNF papers were tested according to Profile 3 (50 mA/g). FESEM and TEM images of the CNF paper (Figures 29 and 30) showed that the CNFs were approximately 70 to 200 nm in diameter and up to 10 microns long. A Raman spectrum taken with a Renishaw inVia microscope and a neodymium-yttrium-aluminum-garnet laser operating at 532nm displayed peaks at 1,308 cm$^{-1}$ and 1,598 cm$^{-1}$ (Figure 31). The 1,598 cm$^{-1}$ peak is near the typical G-band peak of graphite (1,580 cm$^{-1}$), indicating the presence of crystalline carbons. The stronger 1,308 cm$^{-1}$ peak is within the D-bands (1,100 cm$^{-1}$ to 1,500 cm$^{-1}$), which indicates disordered carbons.

The CNF papers produced a maximum specific capacity of 211 mAh/g and 212 mAh/g for two samples after 20 cycles (Figure 32). This exceeds the performance of both the SWNT and MWNT buckypapers, going against the common belief that smaller carbon particles yield superior performance. Both MWNT buckypapers had larger total capacities than the CNF paper, but lost greater amounts during the first cycle charge. Also, unlike the MWNT and SWNT papers, the CNF paper did not exhibit a plateau at 0.8 volts (Figure 33). Instead, the voltage dropped off slowly between 1 volt and 0.02 volts, indicating, as proposed by R. Yazami that the surface of the CNFs is capable of accommodating a more developed SEI, lessening the reduction of the solvent [59].
Thus, the results of the test with the CNF paper indicated that it may have a higher efficiency than the MWNT buckypapers. The best CNF paper finished the tests with an irreversible capacity of 711.06 mAh/g after 20 cycles, versus 824.63 mAh/g for the NCC MWNT buckypaper, and 971.80 mAh/g for the SES MWNT buckypaper. The SES SWNT buckypaper had an irreversible capacity of 662.12 mAh/g. Like the SWNT and MWNT anodes, the CNF paper is likely to have portions become isolated due to the formation of the SEI layer.

TEM images of the CNFs after cycling did not show the SEI layer. Nor did they give any indication of where the lithium intercalated into the CNFs (Figure 34). While it is expected that because of the high irreversible capacity, there should be lithium ions trapped within the CNFs, the lithium is physically very small and may not cause significant deformations in the CNF structure. Lithium is also not detectable by x-ray diffraction or EDS.

X-ray diffraction studies were performed to detect any changes in the CNFs. While no changes were found, these studies indicated the presence of lithium fluoride (LiF) in the CNFs after electrochemical testing (Figure 35). LiF is a component of the SEI layer, formed as the electrolyte breaks down. This strengthens the assertion that the SEI layer is forming on the individual CNFs, electrically isolating some from the rest of the anode, and driving up the irreversible capacity. In fully functioning lithium-ion batteries, other components of the SEI may include Li$_2$Co$_3$, LiCo$_2$-R, and LiO$_2$ [34]. However, these will not be present in the samples used in this research because lithium disks are used in
place of LiCoO$_2$ and the anodes are tested in an argon atmosphere. The peak on the “before” sample at approximately 26 degrees is graphitic. This peak stabilizes after cycling. The rest of the spectra indicate amorphous scatter, most likely from the carbon.

Figure 29. FESEM image of ASI CNF paper.
Figure 30. TEM image of ASI CNF before electrochemical testing.

Figure 31. Raman spectrum of ASI CNFs before electrochemical testing.
Figure 32. Discharge and charge capacities of CNF paper anodes over 20 cycles.

Figure 33. Cycles 1-5 discharge and charge curves for CNF paper.
Figure 34. TEM image of ASI CNFs after electrochemical testing.

Figure 35. X-ray diffraction spectra of ASI CNFs before and after electrochemical testing.
9. TIN-OXIDE NANOPARTICLES

Finally, the performance of the tin-oxide nanoparticles was characterized, since the majority of the anodes’ content will be tin-oxide. The tin-oxide powder was purchased from Sigma Aldrich and had a diameter less than 200 nm (Figure 36). To perform electrochemical tests on the tin-oxide powder, it was combined with graphite powder (Timcal Super P-Li) and polyvinylidene fluoride (PVDF, Sigma Aldrich). A mixture of 0.02 grams tin-oxide, 0.8 grams graphite, and 0.04 grams PVDF was combined in a beaker and mixed by hand with NMP to form a slurry. The slurry was poured onto an 80 mesh copper grid on top of a Whatman #6 cellulose filter, and allowed to dry in a vacuum oven at 125°C for 24 hours. After removal from the oven, the material was electrochemically tested at 50 mA/g while still on the copper grid. The weight of the copper grid was estimated and factored out.

Recalling that the composition of the tin-oxide/graphite/PVDF anode was 0.02 grams tin-oxide, 0.8 grams graphite, and 0.04 grams PVDF, it was theoretically capable of delivering 422 mAh/g of capacity. However, it only made a maximum 23 mAh/g after 20 cycles (Figure 37). The first cycle discharge capacity was 1,823 mAh/g. However, much of this capacity is believed to be due to lithium alloying with copper-oxides on the mesh, since it far exceeds the theoretical capacity of the material. The actual active anode mass was only 2.2 percent of the total test material mass (anode and copper mesh).

Observation of the charge and discharge curves (Figure 38), reveals a steady loss in both charge and discharge capacities over the first five cycles. According to the capacity
chart, the loss continues through the seventh cycle before the reversible capacity stabilizes.

When viewed in the SEM, an additional reason for the poor performance was clear. In the SEM of the tin-oxide/graphite/PVDF anode before cycling, the tin-oxide nanoparticles are visible on the surfaces of the graphite flakes (Figure 39). However, after cycling, the tin-oxide nanoparticles are no longer clearly seen. Instead balls of electrolyte residue are present on the surfaces of the graphite flakes (Figure 40). It is believed that tin-oxide nanoparticles are contained within these objects.

Figure 36. TEM image of Aldrich SnO2 NPs showing the relative sizes of the NPs.
Figure 37. Discharge and charge capacities of an SnO$_2$/graphite anode.

Figure 38. Cycles 1-5 charge and discharge curves for an SnO$_2$/graphite anode.
Figure 39. SEM image of an SnO$_2$/graphite anode before cycling.

Figure 40. SEM image of an SnO$_2$/graphite anode after cycling.
10. RESULTS AND DISCUSSION

10.1. 75% SnO$_2$, 20% SWNT, 5% CNF Bath Sonicated Anode Material

Anodes of 75% SnO$_2$, 20% SWNT, 5% CNF were fabricated by dispersing the materials with a three-hour bath sonication in NMP. After drying and electrochemical testing, it was found that it only had a reversible capacity of 188.75 mAh/g after 20 cycles and repeatability of its performance was poor (Figure 41). A second sample only had a reversible capacity of 139.17 mAh/g, while a third and fourth were even lower at 108.92 mAh/g and 96.80 mAh/g, respectively. Many others demonstrated even lower capacities.

Examination of the first five cycles showed that there was a significant loss of capacity on the first cycle (Figure 42). This loss may be explained by studying an SEM image of the material which shows that large clumps of SWNTs remained after sonication and much of the tin-oxide nanoparticles rested upon the surface of the SWNT clumps instead of being captured by them. (Figure 43). As with the tin-oxide/graphite anodes, it is very likely that the tin-oxide nanoparticles separated from the surface of the SWNT clumps.

The SEM image of the same anode material after 20 discharge/charge cycles (Figure 44), showed the formation of white spheres throughout the anode, similar to the tin-oxide/graphite anodes. The tin-oxide nanoparticles are no longer visible on the surface of the SWNT clumps. It is possible that the spheres are actually the tin-oxide nanoparticles surrounded by residue from the electrolyte. Attempts were made to confirm this with FIB and TEM studies. While not definitive, the studies suggested that
the particles were tin-oxide covered with a substance, most likely electrolyte residue.
The SWNT clumps are likewise covered by a white material, most likely electrolyte residue. In this way, the tin-oxide is separated from the SWNTs and after the first cycle, no longer contributes to the anode’s reversible capacity.

While infiltration of the electrolyte and the consequential formation of the SEI layer on the CNTs may be the main cause of the anode breakdown, this process may be exacerbated by the presence of the tin-oxide particles themselves. In an anode without tin-oxide, the CNTs and CNFs are in better contact with each other. However, when the tin-oxide is present, it causes a physical separation between CNTs and CNFs. In the basic concept behind the anodes described in this work, the CNTs were expected to maintain good contact with each other. It appears that this is not the situation.
Figure 41. Reversible capacity of four anodes containing 75% SnO$_2$, 20% SWNT, 5% CNF dispersed by a three hour bath sonication.

Figure 42. Cycles 1-5 charge and discharge curves for a 75% SnO$_2$, 20% SWNT, 5% CNF anode dispersed by bath sonication for three hours.
Figure 43. SEM image of 75% SnO$_2$, 20% SWNT, 5% CNF anode dispersed by three hour bath sonication.

Figure 44. SEM image of three-hour bath sonicated a 75% SnO$_2$, 20% SWNT, 5% CNF anode after 20 test cycles.
10.2. 50% SnO$_2$, 40% SWNT, 10% CNF Horn Sonicated Anode Materials

To better disperse the SWNTs and allow them to capture the tin-oxide nanoparticles, the sonication process was modified. The sonication instrument was changed to a horn sonicator and the intensity of the processing was increased. A 50% SnO$_2$, 40% SWNT, 10% CNF anode that was dispersed by pulsing the sonicator at 20% intensity for eight seconds on and four seconds off, over a 10 minute duration, produced a maximum reversible capacity of 127.72 mAh/g (Figure 45), slightly less than the average performance of the four best bath sonicated materials. Two other anodes that were horn sonicated for 10 minutes finished their tests with reversible capacities of 55.90 mAh/g and 4.86 mAh/g, indicating severe breakdown in the anode structure. The discharge and charge curves of the 50% SnO$_2$, 40% SWNT, 10% CNF anodes (Figure 46) were very similar to that of the 75% SnO$_2$, 20% SWNT, 5% CNF bath sonicated anodes, however the initial voltage drop is faster with the horn sonicated material.

Since an outright improvement in performance was not gained by a mild increase in the dispersion intensity, the sonication time was changed to 30 minutes and the probe amplitude increased to 39%. The anode content remained 50% SnO$_2$, 40% SWNT, 10% CNF. This yielded a slightly reduced performance compared to the 10 minute sonicated material. The best 30 minute sonicated anode was capable of 101.98 mAh/g after 20 cycles (Figure 45), while two other anodes from the same batch produced 58.08 mAh/g.
Figure 45. Reversible capacity of anodes containing 50% SnO$_2$, 40% SWNT, 10% CNF dispersed by three sonication methods.

Figure 46. Cycles 1-5 charge and discharge curves for a 50% SnO$_2$, 40% SWNT, 10% CNF anode dispersed by horn sonication for 10 minutes, pulsed at 8 seconds on, 4 seconds off.
and 36.52 mAh/g. The discharge and charge curves for this anode (Figure 47) were slightly different from the first two materials in that there was a steeper initial drop in voltage, followed by a broad plateau. While the plateaus of the three anodes are roughly the same length, on the 30 minute sonicated sample the plateau occupies a greater fraction of the first cycle discharge capacity. This may indicate more intense electrolyte breakdown during the formation of the SEI layer. The discharge and charge curves for cycles 2-5 are spread apart and indicate poor efficiency for this anode material.

While the purpose of increasing the sonication intensity was to better disperse the SWNTs, in the SEM, clumps of SWNTs are still visible with the tin-oxide nanoparticles resting upon them (Figure 48). Compared to the three-hour bath sonicated anode, the SWNTs were only slightly better dispersed when they were horn sonicated for 30 minutes. A dispersant (Nanosperse AQ, Nanolab) was briefly used, but abandoned because it clogged the cellulose filter and inhibited the fabrication of the anodes.

Even though the results of the 30 minute sonicated anodes were not encouraging, the sonication time was increased to 60 minutes and the intensity remained at 39%, just below the maximum allowable on the sonicator. Two of these anodes were tested, but the performance decreased further (Figure 45) with one anode only achieving 26.58 mAh/g after 20 cycles and the other, 12.08 mAh/g.

The plateau in the first cycle discharge curve of this anode, while only slightly shorter than the previously discussed plateaus, covered one third of the discharge time (Figure
Figure 47. Cycles 1-5 charge and discharge curves for a 50% SnO₂, 40% SWNT, 10% CNF anode dispersed by horn sonication for 30 minutes.

Figure 48. SEM image of a 30 minute horn sonicated 50% SnO₂, 40% SWNT, 10% CNF anode.
Figure 49. Cycles 1-5 charge and discharge curves for a 50% SnO$_2$, 40% SWNT, 10% CNF anode dispersed by horn sonication for 60 minutes.

Figure 50. SEM image of a 60 minute horn sonicated 50% SnO$_2$, 40% SWNT, 10% CNF anode.
49), perhaps indicating even more electrolyte breakdown. Anomalies were observed in the first and third cycle charge curves of the anode. The reasons for the abnormalities are difficult to determine, but in this case they did not appear to affect the performance of the anode. No problems in the test system were noted. The SEM image of the 60 minute sonicated anode showed uniform dispersion of the SWNTs and less tin-oxide visible on the surface (Figure 50). This was an indication that the tin-oxide nanoparticles were entrapped by the SWNTs as planned. However this did not lead to higher performance.

After completion of the tests with the SnO$_2$-SWNT-CN anodes, a trend emerged. The performance of the anodes deteriorated with the intensity of the sonication process. A partial explanation for the inferior performance of the horn sonicated anodes is that the SWNTs are shortened during the sonication process. The shortened CNTs are unable to entangle as well with each other and the tin-oxide nanoparticles. Also, with the SWNTs being better dispersed, they are less tangled, allowing them to be separated from each other by the electrolyte when the SEI layer forms on the CNTs. The SEI layer is capable of overwhelming the Van der Waals forces between the CNTs and electrically isolates portions of the anode and increases the irreversible capacity. As with the tin-oxide/graphite anodes, the nanoparticles are also separated from the SWNT matrix by the SEI layer.

Further SEM studies showed that the tin-oxide nanoparticles were still not being well captured by the CNTs, allowing them to lose contact with the anode matrix as they attempted to de-alloy from the lithium. This is reflected in high first cycle irreversible
capacities of 2,113 mAh/g, 1,444 mAh/g, and 1,003 mAh/g for the best three 75% SnO$_2$, 20% SWNT, 5% CNF anodes. As previously discussed, it can also be seen most clearly in SEM images of graphite and tin-oxide (Figures 39 and 40). In Figure 39, the tin-oxide NPs are seen on the surface of the graphite before cycling. After cycling (Figure 40), the tin-oxide NPs are no longer visible. Instead, there are several white spheres in locations were the tin-oxide could originally be found. These spheres may be tin-oxide nanoparticles surrounded by electrolyte residue and are seen on many anodes after cycling (Figure 51). The sizes of the denser interior of the spheres are consistent with the sizes of the smaller pristine tin-oxide nanoparticles (Figure 36). The spheres were imaged on a Phillips CM200 Lab 6 TEM, which was not capable of producing an EDX map of the area.

While the same particles could not be found when the material was imaged on the FEI Titan TEM, an EDX mapping of similarly dark particle indicated that they were composed of tin (Figures 52 and 53). Additionally, an EDX scan of the area indicated the presence of fluorine in the anode, along with tin and carbon (Figure 54). It is therefore likely that the fluorine content in the anode was not sufficient to show clearly on the EDX map.
Figure 51. TEM image of SnO$_2$ nanoparticle encased in electrolyte residue.

Figure 52. TEM image of 50% SnO$_2$, 40% MWNT, 10% CNF anode after electrochemical cycling.
Figure 53. EDX map of SnO$_2$ nanoparticle in 50% SnO$_2$, 40% MWNT, 10% CNF anode after electrochemical cycling.

Figure 54. EDX scan of 50% SnO$_2$, 40% MWNT, 10% CNF anode after cycling.
10.3. 50% SnO$_2$, 40% MWNT, 10% CNF Horn Sonicated Anode Materials

Anodes containing MWNTs instead of SWNTs were studied, speculating that they would offer similar performance, but at a lower cost. The anodes were fabricated using the same methods as with the SWNT based anodes. The MWNT based anodes fabricated were 50% SnO$_2$, 40% MWNT, 10% CNF, horn sonicated for 30 minutes and 60 minutes. The reversible capacities for both of these anodes are shown in Figure 53. The best 30 minute sonicated anode was only capable of producing 25.20 mAh/g after 20 cycles. The 50% SnO$_2$, 40% SWNT, 10% CNF anodes were capable of up to 101.98 mAh/g. 50% SnO$_2$, 40% MWNT, 10% CNF anodes sonicated for 60 minutes were not capable of running for more than five cycles. The first five cycle curves for the 30 minute sonicated anode showed instability in the anodes (Figure 56). Likewise, the charge and discharge curves for the 60 minute dispersed anode also showed instability (Figure 57), but not to the degree of the 30 minute sonicated anodes. The instability may be caused by movement of the tin-oxide, CNTs, and CNFs with respect to each other as the tin-oxide grows and shrinks with the alloying and de-alloying with lithium.

The MWNTs dispersed more readily than the SWNTs, and this seemed to degrade their performance. 50% SnO$_2$, 40% MWNT, 10% CNF anodes are shown in Figures 58 and 57, and it can be seen that unlike the SWNTs, the MWNTs are well separated from each other, and there are no large bundles of MWNTs that can beneficially entrap the tin-oxide nanoparticles. In this case, it is also possible that the tin-oxide nanoparticles aid in the separation of the MWNTs. This facilitates the isolation of the anode components from each other because the electrolyte easily penetrates into the anode.
The SEI layer is then capable of forming within the anode, instead of just on the surface. Formation of the SEI within the anode causes portions of the anode to be electrically isolated, increasing the irreversible capacity. As discussed in Section 10.2, SEM and TEM images also show the presence of the white spheres which may be tin-oxide nanoparticles with electrolyte coatings.
Figure 55. Reversible capacity of 50% SnO$_2$, 40% MWNT, 10% CNF anodes horn sonicated for 30 minutes and 60 minutes.

Figure 56. Cycles 1-5 charge and discharge curves for a 50% SnO$_2$, 40% MWNT, 10% CNF anode dispersed by horn sonication for 30 minutes.
Figure 57. Cycles 1-5 charge and discharge curves for a 50% SnO$_2$, 40% MWNT, 10% CNF anode dispersed by horn sonication for 60 minutes.

Figure 58. SEM image of a 50% SnO$_2$, 40% MWNT, 10% CNF anode, horn sonicated for 30 minutes.
Figure 59. SEM image of a 50% SnO$_2$, 40% MWNT, 10% CNF anode, horn sonicated for 60 minutes.
10.4. 75% SnO$_2$, 20% MWNT, 5% CNF Bath Sonicated Anode Materials

A 75% SnO$_2$, 20% MWNT, 5% CNF anode was also fabricated using the three-hour bath sonication method in an attempt to elicit the same type of performance seen in the SWNT based anodes. However, because of the looseness of the MWNT based anodes, this was not possible. The discharge-charge curves (Figure 60) illustrate the large losses in capacity that occur with each cycle and show instability of the anode near the peak voltages. Regarding the irreversible capacities, the MWNT based horn sonicated anodes were only able to generate a maximum of 17.77 mAh/g after 20 cycles, far below the result from the SWNT based anodes (Figure 61).

The SEM images of this anode material show what seems to be an over-abundance of tin-oxide (Figure 62). This did not seem to be the case with the 75% SnO$_2$, 20% SWNT, 5% CNF anode (Figure 43). Therefore, with the MWNT anode, there may actually be a deficiency of MWNTs. For example, a 200mg anode of only MWNTs will contain approximately 7.89x10$^{10}$ nanotubes, while an equal mass SWNT only anode will contain approximately 1.08x10$^{14}$ nanotubes. The SWNT anode will contain over 1,300 times the number of CNTs as the MWNT anode. The greater number of SWNTs will be more capable of suspending the tin-oxide nanoparticles within the anode matrix and yield a higher reversible capacity (Figure 61). Even among MWNT based anodes, the anode with more MWNTs (50% of the anode mass) was capable of generating a comparable reversible capacity to the 75% tin-oxide anode, despite the fact that the theoretical capacity of the 75% tin-oxide anode (1,211 mAh/g) was higher than the 50% tin-oxide anode’s (931.5 mAh/g).
Figure 60. Cycles 1-5 charge and discharge curves for a 75% SnO$_2$, 20% MWNT, 10% CNF anode dispersed by bath sonication for three hours.

Figure 61. Reversible capacities of 75% SnO$_2$, 20% SWNT, 5% CNF and 75% SnO$_2$, 20% MWNT, 5% CNF anodes fabricated by three hour bath sonication and 30 minute horn sonication over 20 cycles.
Figure 62. SEM image of a 75% SnO$_2$, 20% MWNT, 5% CNF anode, bath sonicated for 3 hours.
10.5. Electrolyte Accumulation Study

A brief study was executed to observe the progression of the electrolyte buildup in the anodes. This was done with a 50% SnO$_2$, 40% SWNT, 10% CNF anode, electrochemically tested for 1, 2, 5, and 20 cycles. The cycled anodes were cleaved and mounted in the SEM so that their internal structure was visible from the side. This was a more expedient alternative to using the FIB. Images from these anodes are presented in Figure 63 to document the progression of the electrolyte buildup in the anodes.

While the SEI itself is very difficult to capture in an image – it can only be seen on the TEM, and the sonication necessary to prepare the sample often destroys the SEI – we can assume that because of the presence of the electrolyte, the SEI does in fact form on the CNTs. Recall that others have documented the effects of this phenomenon and noted that it leads to electrical separation of fractions of the anode particles from the current collector [34,34,59]). It can be seen that the electrolyte steadily accumulates as the anode is cycled. By five cycles, the buildup of the electrolyte within the anode is nearly complete. This coincides with the point at which the reversible capacity of many of the anodes levels off.

To counter the effects of the formation of the SEI layer, phenolic resin (Durite SC-1008, Hexion Chemicals) was added to the anodes and carbonized in order to bind the SWNTs to the tin-oxide nanoparticles and to each other. The hard connections between the nanomaterials would ensure that the integrity of the anode was maintained despite infiltration of the electrolyte.
Figure 63. SEM images of a 50% SnO$_2$, 40% SWNT, 10% CNF anode after 0, 2, 5, and 20 cycles (left to right).
10.6. Carbonized Anodes

As previously discussed, when the SEI layer forms within the anode, it is believed that it coats the individual anode components, electrically isolating a majority of them. It was believed that the addition and carbonization of a phenolic resin would bind the CNTs, CNFs, and tin-oxides nanoparticles together and mitigate the effect of the formation of the SEI layer.

The first carbonized anodes were fabricated by infiltrating thinned resin (Durite SC-1008 Hexion Chemicals) into the material, a process borrowed from the composites world. These anodes were 50% SnO$_2$, 40% SWNT, 10% CNF, sonicated for 60 minutes. The process to infiltrate the resin into the anodes is as follows:

1. The resin was thinned with acetone to the specified viscosity.
2. The pristine anodes were placed in vacuum chamber, specifically made for the process.
3. Air was pumped out of the chamber, and the anodes within it.
4. The thinned resin was poured onto the anodes.
5. After the resin covered the anodes, the air was reintroduced into the chamber. This forces the resin into the anodes.
6. Depending on the viscosity of the resin, it is allowed to infiltrate into the anodes for three to six hours.

After carbonizing the anodes in argon at 1,000$^\circ$C, the anodes were electrochemically tested. These anodes, infiltrated with resins with acetone to resin ratios of 10:1, 20:1, 30:1, and 40:1 showed no improvement over the pristine anodes. Anodes infiltrated
with full-strength resin were also tested. Each of the anodes failed to produce a reversible capacity greater than 30 mAh/g (Figure 64) and the full-strength resin anode that completed the electrochemical test showed erratic performance in the first few cycles. Examination of the SEMs of the carbonized anodes showed the presence of hard carbons that do not allow easy penetration of the electrolyte (Figure 65). Penetration of the electrolyte is required for transport of the lithium ions throughout the anode.

Since the carbonized anodes made by infiltration failed to deliver an improvement in the anodes capacity to store and release lithium ions, a new method was created to carbonize them. The dispersant was changed to acetone and the resin was added to it. The materials were then horn sonicated for 60 minutes at 40% amplitude. The intention was to have the resin deposit onto the tin-oxide, SWNTs, and CNFs with the excess resin remaining suspended in the acetone. The excess resin would be removed in the filtering process. Noting that the best performance came from anodes with 75% tin-oxide, the anode composition was reverted to 75% SnO$_2$, 20% SWNT, 5% CNF.

During the fabrication of these anodes, it was observed that after the dispersed mixture was removed from the sonicator, the nanoparticles were attracted to the resin and formed precipitates. These precipitates were easily filtered and fused into a contiguous paper during the curing process. These resin imbued anodes were carbonized in the same manner as the infiltrated anodes (Figure 66).
Figure 64. Reversible capacity of anodes infiltrated with phenolic resin over 20 cycles.

Figure 65. SEM image of a carbonized anode infiltrated with a 30:1 acetone to resin mixture. Note the presence of hard carbons within the matrix.
Compared to the pristine 75% SnO$_2$, 20% SWNT, 5% CNF anodes fabricated by 60 minute sonication, the resin imbued anodes had improved performance. However, they were still inferior to the three-hour sonicated anodes (Figure 67). Also of interest is that the performance of the anodes is sensitive to the resin content in the acetone. Anodes dispersed in a 25:1 (3.8%) acetone/resin mixture reached capacities of 131.91 mAh/g and 97.33 mAh/g after 20 cycles. However, of the several anodes dispersed in acetone with 1% resin, the best was only capable of achieving 33.40 mAh/g reversible capacity after 20 cycles.

The resin imbued anodes were showed improvement because they successfully brought the anode components back into contact with each other. However, they were not completely successful because after the carbonization process, SEM images revealed that the hard carbons had separated from the SWNTs and formed distinct orbs which dangled from the SWNT bundles. This highlights the need for improved resins or functionalized CNTs that facilitate the bonding of resins to them.

Since the bath sonicated anodes and the anodes sonicated in an acetone/resin mixture gave the best performance, the methods were combined in an effort to fabricate an anode that outperforms the anodes produced by each individual method. Thus, a mixture of 75% tin-oxide NPs, 20% SWNTs, and 5% CNFs was dispersed in acetone with four percent resin by bath sonication for three hours. However this attempt was also unsuccessful and inferior to both parent methods, only producing 10.81 mAh/g reversible capacity (Figure 67).
Figure 66. SEM image of carbonized 75% SnO$_2$, 20% SWNT, 5% CNF imbued with a 25:1 acetone to resin mixture.

Figure 67. Reversible capacities of 75% SnO$_2$, 20% SWNT, 5% CNF anodes fabricated by bath sonication, 60 minutes of horn sonication, and sonication in an acetone/resin mixture.
Other methods were used in attempts to improve the integrity of the anodes and boost the reversible capacity. These included the addition of PVDF, an often used method. Also attempted was uncarbonized resin and functionalization of the CNTs by heating them in NMP for 24 hours at 200°C. Each of these failed to generate any improvement in the anodes’ performance and often lead to erratic behavior that was witnessed in the discharge-charge curves.
10.7 Necessity for CNFs in Anodes

The final study performed under this effort was to determine if the CNFs are a necessary component and contribute to the performance of the anodes. Anodes were fabricated with 50% SnO$_2$, 50% SWNT and 50% SnO$_2$, 50% MWNT. These anodes were tested in the same manner as all the previous anodes to yield data on the reversible and irreversible capacities as well as to observe their efficiency. Their performance was compared to 50% SnO$_2$, 40% SWNT, 10% CNF anodes and 50% SnO$_2$, 40% MWNT, 10% CNF anodes.

In each of the tests performed, the anodes containing CNFs performed significantly better than the anodes without them. Figure 68 compares the performance of tin-oxide-SWNT-CNf anodes and tin-oxide-SWNT anodes. The best performing 60 minute horn sonicated tin-oxide-SWNT-CNf anode completed the test with a reversible capacity of 26.58 mAh/g while the tin-oxide-SWNT-anode completed its test with a 7.93 mAh/g capacity. Recall that 60 minute sonicated anodes performed very poorly because the CNTs are more loosely bound and susceptible to separation by the electrolyte and the SEI layer. In anodes fabricated by a 10 minute sonication (8 second on, 4 seconds off), the materials containing CNFs again outperformed the materials without CNFs. SWNT based anodes with CNFs had a maximum reversible capacity of 127.72 mAh/g, while the anodes without CNFs had a maximum reversible capacity of 8.53 mAh/g. The tin-oxide-SWNT and tin-oxide-MWNT anodes were also more brittle than the anodes containing CNFs, making them more difficult to handle. Because of their length and large
diameters, the CNF contribute structural integrity to the anodes. The CNFs did not make a significant contribution to the electrical characteristics of the anodes. Resistance measurements of the anodes and resistance model results (discussed in Chapter 11), confirmed this behavior.
Figure 68. Comparative performance of anodes with 50% SnO$_2$, 50% SWNT and anodes with 50% SnO$_2$, 40% SWNT, 10% CNF compositions.
10.8 Discussion of the Irreversible Capacity

The experimental anodes tested in this research exhibited very high irreversible capacities, with most of the loss experienced on the first cycle. The irreversible capacity is tied to the formation of the SEI layer due to electrolyte decomposition. In turn, many have proposed that there is a correlation between the amount of SEI layer formed and the specific surface area (SSA) [107]. Figure 69 shows the average irreversible capacity of various anodes tested in this research, plotted against the SSA. The SSA was calculated based on the specifications of the materials used in the anodes for an anode that was 14.3 millimeters in diameter and 100 microns thick. In the SnO$_2$, CNT, CNF anodes and the 50% SnO$_2$, 50% CNT anodes, there is a definite correlation between the SSA and the irreversible capacity. The same is true for the 100% CNT and CNF anodes.

Also of interest in these anodes, is that the total capacity (the first cycle discharge capacity) often exceeded the theoretical capacity of the materials. A portion of the total capacity may be due to the presence of oxides on the surfaces of the current collectors. While the current collectors were cleaned and polished with steel wool to minimize the amount of oxide present, any oxides on the current collector surfaces will alloy with the lithium and contribute to the irreversible capacity.

Despite the good correlation between the SSA of the anodes and their reversible capacity among the distinct anode types, the correlation is not universal. For example, although the 100% SNWT anode possesses the greatest SSA, its irreversible capacity is not the largest. In a published work by Beguin et al. [108] it is proposed that the active
surface area (ASA) of the anodes correlates better to the irreversible capacity than does the SSA. The ASA corresponds to the total surface area of defects in the materials instead of the BET specific surface like the SSA. Therefore, following the Beguin model, one can assume that the SnO$_2$, CNT, CNF anodes possess higher ASAs, which leads to a larger amount of SEI formation than the other anodes and larger irreversible capacities. Why then do the 50% SnO$_2$, 50% CNT anodes display the lowest irreversible capacities? Upon examination of the first cycle data of these anodes, it can be seen that the discharge capacities of these anodes fail to reach the theoretical capacities of the anodes (932 mAh/g). The 50% SnO$_2$, 50% MWNT anodes have an average first cycle discharge capacity of 605 mAh/g while the 50% SnO$_2$, 50% SWNT anodes have an average first cycle discharge capacity of 832 mAh/g. These anodes were inferior at the onset, unable to provide electron transport completely throughout the material. Therefore, portions of the anodes did not participate in the electrochemical reactions. This is consistent with the fact that the 50% SnO$_2$, 50% CNT anodes were the poorest performers.
Figure 69. Irreversible capacity of battery anodes versus their specific surface areas.
11. PREDICTION MODELS

11.1 Mechanistic Model

Electrical isolation of the anode components was simulated with a mechanistic model. The model consists of CNTs, CNFs, and tin-oxide nanoparticles. At the beginning of electrochemical cycling, the anode components are in good contact with each other, making electron transport possible throughout the anode (Figure 70a).

As the anodes are cycled, the SEI layer forms on the surfaces of each of the anode components (Figure 70b). The SEI layer allows ionic transport, but not electrical transport. Additionally, by the fifth cycle, large depositions of electrolyte precipitates are formed within the anodes (Figure 63).

To mitigate the breakup of the anode due to SEI formation, a phenolic resin can be used to bind the CNTs, CNFs, and tin-oxide nanoparticles together (Figure 70c). The phenolic resin was more effective when it was dispersed in the sonication mixture with the anode components instead of infiltrating it into the anodes. The resin was cured and carbonized after the anode material was filtered.
Figure 70a. CNTs are intended to hold the tin-oxide in place while acting as conductive channels for them.

Figure 70b. During electro-chemical cycling, the SEI layer forms on the anode components, isolating them from each other.

Figure 70c. Adding a phenolic resin to the anodes and carbonizing them is performed to bind the particles together and resist break-up due to the SEI formation.
11.2 Resistance Prediction Model

One of the assumptions behind the anodes is that the inclusion of CNFs would aid electrical conduction through the anode. However, resistance measurements of anodes before electrochemical testing showed that there was little difference between the resistances of anodes with and without CNFs. Also, the anodes are fabricated in small batches and there is a large amount of variability in the performance of the anodes. A resistance prediction model was developed to help determine if there is in fact a lowering of the anode resistance due to the addition of CNFs. A secondary reason for the model is that it was noted during the course of experimentation on the anodes, samples with resistances above 6 ohms were more likely to fail during electrochemical testing. The model could be used to determine if an anode being fabricated exceeded this level of electrical resistance.

The model was built in Microsoft Excel. Values for the SWNT, MWNT, tin-oxide, and silicon resistances were obtained from published data. However, the values for the CNF resistance and the contact resistances were obtained by measuring the resistance of completed anodes and adjusting these values until the correct result was calculated.

Parameters for the anode material under consideration are entered on the first worksheet (Figure 71). Next, three worksheets calculate the quantity and total volume of each of the anode constituents. These values are returned to the first worksheet to calculate to percentage of each constituent in the anode, by volume. The percentages were entered into four worksheets which contain a matrix of cells in 26 columns and
12,000 rows, for a total of 312,000 cells. Each cell represents a single CNT, CNF or tin-oxide nanoparticle and is first populated by a random number from 0 to 1. Knowing that the probability that one of the nanoparticles occupies a particular location follows the normal distribution, this random number is used to place an anode component randomly into each cell. The selection of the component is weighed by the percentage of the component used in the sample. For example, if the random number in the cell is between 0 and 0.5 and the percentage of tin-oxide in the anode is 50%, tin-oxide is placed into the cell. If the random number in the cell is between 0.5 and 0.9 and the CNT content is 40%, a CNT will be placed into the cell. The randomness of the component reflects the random orientation of the components of actual anodes. However, because of their larger diameters and lengths, CNFs were manually entered in multiple complete rows (Figure 72). An appropriate resistance for each constituent in each cell is substituted into the matrix, along with the contact resistances between adjacent constituents (Figures 73 and 74). The sub-total of the resistance is calculated in series for each column, then in parallel for these sub-totals. It is understood that electron transport through the anode is more complex than represented in the model; however the resistance was only calculated vertically in order to keep the model simple. Also, since the matrix represented only a small portion of the anode, the total resistance was scaled up to represent a complete test anode. The final results are presented on the first worksheet, (Figure 71). The actual measured resistances of the anode materials are also given in this table. These resistances were obtained by mounting the anode sample in the same manner as a sample for electrochemical testing (Figure 6), however
the electrolyte, separators, and lithium disk are not used. The resistance was measured with a Fluke multimeter. The measured resistances varied according to the sonication method and time, therefore a range of measured resistances is given where the data was available.

Several runs of the resistance model were made for different anode compositions. Table 4 shows the estimated resistances of anodes of various compositions. The estimates revealed that the change in resistance between anodes with and without CNFs is within the range of resistances of fabricated anodes. The estimated resistance of tin-oxide/SWNT anodes with CNFs was slightly higher than those without CNFs, but the resistance of tin-oxide/MWNT anodes with CNFs was slightly lower than those without CNFs.

Because the anodes with CNFs did not perform electrochemically better than anodes without CNFs (see section 10.7), they are contributing to the anode performance in another way. It is proposed that the CNFs benefit the anodes by increasing their physical integrity. Recalling the images in Figure 7, the anodes with CNFs were apparently stronger and, while brittle, showed less tendency to crumble. On the other hand, the anodes without CNFs were more delicate and could not be handled with tweezers, lest they be crushed in their grasp. Following electrochemical tests, the anodes with CNFs were able to be removed from the electrodes mostly intact, while the anodes without CNFs were reduced to a powder. Therefore, one can infer that the anodes with CNFs exhibit superior electrochemical performance because the CNFs help
maintain the physical integrity of the anodes and thus their electrical integrity. Once anode portions are isolated from the rest of the anode, they may no longer contribute to the reversible capacity.

Table 4. Estimated Resistance of Anode Compositions Calculated by Resistance Model

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<thead>
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<th>Tin-Oxide %</th>
<th>SWNT %</th>
<th>MWNT %</th>
<th>CNF %</th>
<th>Estimated Resistance (ohms)</th>
<th>Measured Resistance (ohms)</th>
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<td>0</td>
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</table>

† Samples crumbles, making resistance measurement difficult

* Model is not set up to perform this calculation.
Figure 71. Input, calculation, and results page of resistance model showing estimated resistances in the anodes.

Figure 72. Resistance model matrix of anode constituents.
Figure 73. Resistance model worksheet showing matrix of resistances for each element.

Figure 74. Resistance model worksheet showing matrix for contact resistances between elements.
11.3 Prediction of Reversible Capacity of Anodes

In order to develop the ability to predict the reversible capacity for the type of anode discussed in this thesis, a multivariate prediction model was developed. This model can be used in the design of experiment to help determine the composition of anodes to be fabricated. Its use can be both a cost and time saver by allowing a person to focus only on anodes that will produce the desired results.

The model is based on the regression equation obtained from multivariate analysis of the test variables. The independent variables used in the regression analysis were the bath sonication time, the horn sonication time, tin-oxide content, SWNT content, MWNT content, and maximum test voltage. The dependent variable was the reversible capacity of the anode. The CNF content was highly correlated to the SWNT and MWNT content and was excluded from the model. Data from anodes containing phenolic resin and PVDF were also excluded. The regression equation was:

\[
\text{Reversible Capacity} = 170.01 - 0.3097\times\text{BathSonicTime} - 0.8547\times\text{HornSonicTime} + 3.0058\times\text{SnO}_2 - 3.1501\times\text{SWNT} - 3.1708\times\text{MWNT} - 42.984\times\text{Voltage}
\]

A constraint of the equation is the voltage must be from 2 to 3 volts. Additionally, a single bath sonication figure was used in the model development, 180 minutes. The flexibility of the regression can be increased with the addition of experimental data to the analysis. The model favors lower processing times and test voltages, as well as higher tin-oxide content to obtain the highest reversible capacity (Figures 75 and 76).
When the test voltage was 2 volts, the predicted reversible capacity for an anode with 75% SnO\textsubscript{2}, 20% SWNT, 5% CNF, sonicated for 5 minutes was 240 mAh/g, exceeding that of the best anode that was fabricated (189 mAh/g). The model predicted that MWNT based anodes would perform similarly to the SWNT based anodes. The predicted reversible capacity for an anode with 75% SnO\textsubscript{2}, 20% MWNT, 5% CNF was 242 mAh/g with a 2 volt test voltage. In the experiments no anode was tested to confirm this performance. However, a 50% SnO\textsubscript{2}, 20% MWNT, 5% CNF anode, sonicated for 60 minutes was fabricated and produced a low reversible capacity of 12 mAh/g when tested at 3V. The model predicted that such an anode would have a reversible capacity of 13 mAh/g. This suggests an acceptable level of fidelity within the model and indicates that MWNT anodes may perform as well as SWNT anodes.
Figure 75. Multivariate model predictions of anode performance for SnO$_2$-SWNT-CNFMWNT-CNF anodes.

Figure 76. Multivariate model predictions of anode performance for SnO$_2$-MWNT-CNFMWNT-CNF anodes.
12. SUMMARY AND CONCLUSIONS

12.1. Analysis of Results

With the completion of the tests with the SnO$_2$-SWNT-CNFS anodes and the SnO$_2$-MWNT-CNFS anodes, the following determinations were made:

1. The nanoparticles were the primary lithium storage media: In the 75% SnO$_2$, 20% SWNT, 5% CNF anodes the maximum contribution from the CNTs and CNFs is 92.9 mAh/g, however the first cycle discharge capacities of the anodes routinely exceeded 2,000 mAh/g. While in test conditions, lithium-ion battery anodes often exceed their theoretical capacities, it is not by such a large factor.

2. The CNTs were only capable of transporting electrical current to and from the nanoparticles efficiently over the first few discharge/charge cycles: Proper function within the anode depends upon good ionic transport and electrical transport. Since SEM images show that the electrolyte penetrates well into the anodes, thus facilitating ionic transport, electrical connections within the anode are likely failing. Electron transport only functioned at its best capacity on the first cycle discharge.

3. The CNTs did not remain in contact with the nanoparticles and accommodate their volume changes: As discussed previously, the SEI layer overcomes the Van der Waals forces that keep the tin-oxide nanoparticles in contact with the SWNTs. Therefore, when the tin-oxide nanoparticles attempt to de-alloy with the lithium, they shrink and lose contact with the SWNTs, resulting in high irreversible losses.
4. MWNTs did not function as well as SWNTs in the anodes: In almost all the experiments conducted, the MWNT based anodes performed in an inferior manner to the SWNT based anodes.

5. The CNFs did not significantly improve electron transport from the CNTs to the current collectors of the cell: This was determined with the resistance model and direct measurements of anodes. However, the CNFs were beneficial because they improved the physical integrity of the anodes, allowing the anodes containing them to demonstrate superior reversible capacity than anodes without CNFs.
12.2. Conclusion

An extensive study has been performed on a novel anode material for lithium-ion batteries. The data indicate that the material may be capable of high reversible capacities, however internal degradation of the anode currently limits this. The formation of the SEI layer throughout the anode and on the individual particles is suspected to be the cause of the degradation. Normally, the anode is held together by Van der Waals forces between the particles. The SEI layer formation overcomes the Van der Waals forces and pushes the particles apart. Additionally, the SEI is not electrically conductive. The greatest loss of capacity occurs on the first cycle of anode tests, coincident with the formation of the bulk of the SEI layer. This behavior was seen not only in anodes with tin-oxide, CNTs, and CNFs, but also in anodes with only one constituent. Evidence of the formation of the SEI was found in x-ray diffraction studies which detected the presence of LiF, a component of the SEI.

Several contributions were made to the body of knowledge of lithium-ion battery anodes. These include:

- Two peer-reviewed journal articles: “Improving Anodes for Lithium-Ion Batteries” (Metallurgical and Materials Transactions A, 42 (2011) 231-238), and “Silicon-Coated Carbon Nanofiber Hierarchical Nanostructures for Improved Lithium-Ion Battery Anodes” (Journal of Power Sources, 196 (2011) 10254-10257).

- A model to predict anode resistance, a potential indicator of premature anode failure.

- A multivariate model to estimate the reversible capacity of buckypaper anodes.
A mechanistic model illustrating anode degradation with the formation of the SEI layer.

An extensive study on a novel ternary material for lithium-ion battery anodes.

In this research, several attempts were made to maintain the physical integrity of the anodes. These included the addition of PVDF, altering the sonication times, and the addition of phenolic resins. Adding a phenolic resin and carbonizing the anode yielded the best results, provided that the anodes materials were sonicated in acetone with the resin in it. During the fabrication of the anodes, the resin caused clusters of anode material to be formed in the acetone. These clusters fused into a contiguous material as it was filtered and cured. These clusters are believed to bring the anode constituents into contact with each other.

If the resin was added by infiltration after the anode was fabricated, there was no improvement in performance. With the infiltrated anodes, the hard carbons were observed on the SEM. These hard carbons inhibit the penetration of the electrolyte into the anode and thus limit ionic transport within the anode.

The data indicated that the best anode performance was obtained with the lowest processing intensity. That is, anodes that were bath sonicated for three hours had the best reversible capacity. Anodes that were horn sonicated for 10 minutes (pulsed for eight seconds of sonication, four seconds without sonication) gave the next best performance. The reversible capacity steadily fell off as the sonication time was increased. SEM images showed that the longer sonication times created more dispersed materials, as expected. CNT lengths are also reduced during sonication. Both
these factors work together to create an anode with components that are not as tangled as the bath sonicated materials. The less tangled materials are more easily separated by the SEI layer.

It was also discovered that SWNT-based anodes were capable of higher reversible capacities than MWNT-based anodes. SEM images revealed that the SWNT-based anodes contained bundles that remain in better contact with each other and may trap tin-oxide within them. The MWNTs were more easily dispersed and were more susceptible to separation by the SEI layer.

The importance of CNFs in the anodes was studied. Resistance measurements of the anodes were inconclusive because the resistances varied depending on the anode sonication time. A resistance model was created to estimate the resistance of anodes. The results of the model fell within the measured resistances of the anodes and did not consistently reduce the resistance of the anodes. This indicated that the CNFs did not significantly contribute to the electrical performance of the anodes. However, subjectively, anodes with CNFs were more robust than anodes without CNFs. Anodes without CNFs, particularly MWNT-based anodes, were more brittle than anodes with CNFs. Therefore, it is proposed that the CNFs aid in maintaining the physical integrity of the anodes during electrochemical testing.
13. FUTURE WORK

Future work can entail the exploration of other binding mechanisms. These may include epoxies such as Novolac epoxy resin. Novolac has been used in ball-milled anodes to prevent formation of silicon carbide, but not yet as a carbonizing agent. Another promising technique to improve anode performance is spark plasma sintering, a process developed by K. Yang, et al at Clemson University [34]. This technique fuses the walls of multi-walled CNTs together under pressure in order to make a dense, highly conductive material. The spark plasma sintering process may be modifiable to fuse the CNTs together without applying pressure. Fusing the CNTs together where they touch may overcome the effects of the SEI layer growth on the CNTs. This process has not yet been performed SWNTs, and this will have to be explored. Additionally, it is not known if spark plasma sintering will also fuse the tin-oxide or silicon nanoparticles to the CNTs and CNFs. If the technique is successful, it may allow MWNTs to be successfully substituted for SWNTs.
## APPENDIX A – ANODE TEST COMPILATION

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<th>Date</th>
<th>Run Number</th>
<th>Shear Mixer Time</th>
<th>Bath Sonic Time</th>
<th>Horn Sonic Time</th>
<th>SnO₂ %</th>
<th>Si %</th>
<th>SWNT %</th>
<th>MWNT %</th>
<th>CNF %</th>
<th>Graphite %</th>
<th>Infiltrated Resin %</th>
<th>Mixed in Resin %</th>
<th>PVDF %</th>
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