Sustainability impact of nanomaterial enhanced lithium ion batteries

Matthew Ganter

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SUSTAINABILITY IMPACT OF NANOMATERIAL ENHANCED LITHIUM ION BATTERIES

by
Matthew Ganter

IN PARTIAL FULFILLMENT OF DISSEPTION EXAM

For the degree of Doctor of Philosophy in Sustainability at the Rochester Institute of Technology Department of Sustainability Golisano Institute for Sustainability

June 6, 2013

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ABSTRACT

Energy storage devices are becoming an integral part of sustainable energy technology adoption, particularly, in alternative transportation (electric vehicles) and renewable energy technologies (solar and wind which are intermittent). The most prevalent technology exhibiting near-term impact are lithium ion batteries, especially in portable consumer electronics and initial electric vehicle models like the Chevy Volt and Nissan Leaf. However, new technologies need to consider the full life-cycle impacts from material production and use phase performance to the end-of-life management (EOL). This dissertation investigates the impacts of nanomaterials in lithium ion batteries throughout the life cycle and develops strategies to improve each step in the process.

The embodied energy of laser vaporization synthesis and purification of carbon nanotubes (CNTs) was calculated to determine the environmental impact of the novel nanomaterial at beginning of life. CNTs were integrated into lithium ion battery electrodes as conductive additives, current collectors, and active material supports to increase power, energy, and thermal stability in the use phase. A method was developed to uniformly distribute CNT conductive additives in composites. Cathode composites with CNT additives had significant rate improvements (3x the capacity at a 10C rate) and higher thermal stability (40% reduction in exothermic energy released upon overcharge). Similar trends were also measured with CNTs in anode composites. Advanced free-standing anodes incorporating CNTs with high capacity silicon and germanium were measured to have high capacities where surface area reduction improved coulombic efficiencies and thermal stability. A thermal stability plot was developed
that compares the safety of traditional composites with free-standing electrodes, relating the results to thermal conductivity and surface area effects.

The EOL management of nanomaterials in lithium ion batteries was studied and a novel recycling technique, referred to as *refunctionalization*, for lithium ion cathode materials was developed. *Refunctionalization* is the treatment of active materials in order to regain electrochemical performance at EOL which eliminates the need to recycle to the elemental level and can lead to greater environmental and economic savings. The lithium ion capacity of EOL lithium iron phosphate (LiFePO₄) nanomaterial cathode was regained through chemical and electrochemical re-lithiation techniques. The embodied energy of refunctionalized LiFePO₄ was calculated to be 50% less than cathode synthesized from virgin materials.

Overall, these results contribute to an improved understanding of the life cycle impacts for nanomaterials in batteries. The CNT embodied energy calculation established the first life cycle inventory for laser vaporization CNTs, whereas the novel *refunctionalization* strategies established a new EOL pathway to recover cathodes at a higher value state than traditional recycling. At the same time, CNT enhanced battery electrodes increased power and energy in the use phase while demonstrating the unique ability to engineer electrodes to control thermal stability, which enables better performing and safer batteries.
Acknowledgements

First, I would like to thank my committee members for their support and guidance through the completion of my Ph.D. degree in Sustainability.

Advisor: Dr. Brian Landi

Committee: Dr. Ryne Raffaelle, Dr. Gabrielle Gaustad, Dr. Callie Babbitt

Professor’s Gaustad and Babbitt, I truly enjoyed the classes I took with you both and found them extremely valuable for my education in sustainability. You are both excellent mentors and stewards for the program.

I want to thank Dr. Raffaelle for the opportunities he afforded me and his guidance in my development in education and research. I am glad I was able to have Dr. Raffaelle on my committee and was able to keep in touch both at and outside of RIT through these years.

Dr. Landi was an amazing advisor, and was hands on in his guidance of my research and development. I cannot thank Dr. Landi enough for his patience in developing my research path and accomplishments. I would like to thank Dr. Landi for all of his support and comradery both at and outside of work.

I would also like to thank all of my NPRL co-workers for their support, helpful discussions, and trips to Macgregor’s. I would like to particularly thank Chris Schauerman, Roberta Dileo, Jamie Rossi, Annick Anctil, Andrew Bucossi, Michael Forney, Jason Staub, Andrew Merrill, Nate Cox, Chris Bailey, and Cory Cress.

I want to thank all of my family and friends for listening to me ramble about my research and at least pretending to be interested. I have too large a family to list but I love and thank you all. For my friends outside of NPRL, I’d like to thank Chris Zdep, Rob Sliker, Garett Hayes, Rick Hulbert, Joel Raycraft, Sara Forsythe, Jim Stanczyk, Chris Scerbo, and Brandon Redder.

I want to thank my brother, Jeremy, for toughing me up as a kid and always allowing me to hang out even though I was a hyper child. I believe we have become friends along with being brothers as the years have gone by.

I would like to thank my parents, Jamie and Terri, for all of their love and support throughout the years. You have been the best role models a son could ask for, and I am so blessed to have you as my parents.

Finally, I would like my wife Katie for her unwavering support, motivation, love, and friendship. I cannot thank you enough for the sacrifices you made in order for me to graduate and be where I am today.
INTRODUCTION

Energy Storage and Sustainability

Energy storage is considered an integral technology in enabling widespread adoption of sustainable energy and transportation [1-3]. Sustainable energy systems, such as solar and wind, rely on variable and uncertain sources of power generation, and are enhanced by pairing with energy storage systems to increase reliability of power distribution [4]. A primary pathway toward sustainable transportation is through the increased electrification of vehicles to increase efficiency and reduce fossil fuel usage which directly relies on energy storage technologies[5].

Sustainable energy and transportation technologies can be defined as:

“A dynamic harmony (immutability) between the equitable availability of energy-intensive goods and services to all people and the preservation of the earth for future generations.”[6].

This definition is in line with the Bruntland Commission definition of sustainable development which “meets the needs of the present without compromising the ability of future generations to meet their own needs”, and can be applied toward energy storage technologies as well [7]. Energy storage can meet the defined state of dynamic immutability, in which the energy-derived benefits can evolve rapidly to meet ever changing device usage and energy sources. Improving the performance of energy storage devices has implications towards the overarching sustainability goals of reducing the use of natural resources and greenhouse gas (GHG) emissions through electrification of vehicles and renewable energy storage [3, 8]. However, the full life cycle must be taken into account to holistically understand the environmental impacts
and toxicity of the materials used, the costs and benefits in the use phase, and the end-of-life implications which are all important research areas to ensure the sustainability of a technology. Societal concerns must also be considered which include the safety and disruptive nature of the device which effects the ability of the technology to meet the sustainability “triple-bottom line” of balancing environmental, economic, and societal impacts [9].

The 2011 U.S. energy use flow diagram in Figure 1 demonstrates the impact energy storage can have on fossil fuel usage and energy efficiency. Currently, 71% of petroleum is used for transportation and only 25% of the energy is actually converted into usable energy. This demonstrates the reliance on the internal combustion engine which consumes non-renewable petroleum and is restricted by Carnot efficiencies [10].

![Energy flow chart of U.S. energy use in 2011](image)

**Figure 1.** Energy flow chart of U.S. energy use in 2011 (General use reproduction allowed by Lawrence Livermore National Laboratory and Department of Energy).
The transportation sector is the single largest consumer of energy among the four sectors, accounting for nearly 40% of the energy consumed. The efficiency of electric energy storage technologies and the electric motor can improve transportation well-to-wheel efficiency reducing the overall energy consumed. The well-to-wheel efficiencies depend on the electricity source but, even when the electricity is coal or natural gas sourced, a 10-20% efficiency increase has been calculated [11]. However, the efficiency is more than doubled when the electricity is renewably sourced[11]. The use of energy storage for transportation can also provide security and economic benefits through reduced reliance on imported oil [12, 13].

The use of energy storage technologies to improve sustainable transportation efficiency can also reduce environmental impacts by lowering GHG emissions [14]. It is now widely agreed upon within the scientific community that the extensive use of fossil fuels, which results in GHG emissions, is a primary reason for an unprecedented rise in global temperatures[15]. The carbon dioxide emissions trend directly with the energy use as seen in the carbon dioxide flow diagram in Figure 2. Transportation accounts for 33% of the overall U.S. carbon dioxide emissions, and a reduction can contribute significantly towards goals of atmospheric CO₂ stabilization[16].
Figure 2. Energy-related U.S. carbon dioxide emission flows in 2010 (General use reproduction allowed by Lawrence Livermore National Laboratory and Department of Energy).

A variety of energy storage technologies exist such as batteries, capacitors, pumped hydro, and compressed air. Pumped hydro and compressed air are considered good candidates for renewable energy based on their large capacity and low cost\[17\]. However, batteries and capacitors are typically better suited for portable applications due to their high energy and power densities \[18, 19\]. The most promising and wide-spread battery technology for electric vehicles are lithium ion batteries \[20\]. Significant improvements in energy and power density have allowed production of partial or full electric vehicles to greatly increase over the past decade\[21\]. However, even further gains are needed in energy and power density, cycle life, cost, and safety to meet societal demands of range, fast charge, and long life\[22\]. The use of nanomaterials and nanoscaled structures has been at the forefront of improving battery performance. Significant gains in the electrochemical performance of battery materials have been made using
nanomaterials by enabling faster ionic conduction for improved rate capability and stability of active materials with cycling[23, 24]. While much of the focus is on decreasing the size of active cathode and anode particles to the nanoscale, improved rate capability, cycling, and energy density has also been realized through the use of highly conductive and lightweight nanomaterials as conductive additives or free-standing electrode supports[25].

Electrochemical performance is an important factor towards achieving overarching sustainability goals, but the impact of the nanomaterials throughout the battery life-cycle is also needed to fully understand the ultimate sustainability of the battery. Nanomaterial production can be energy intensive and should be monitored in order to justify use in an energy storage technology[26]. In the use phase, not only should the battery performance be measured, but the safety and thermal stability of the battery as well. The effect of these next generation nanomaterials on battery thermal stability is not well understood and is an important factor towards their wide-spread adoption[27]. Also, at the battery end-of-life, strategies to recycle and recover these valuable nanomaterials could reduce their release into the environment as well as eliminate the initial production energy[28]. This work will investigate the sustainability impacts for two prominent nanomaterials in lithium ion batteries in different stages of the battery life cycle.
**Lithium Ion Batteries**

Conventional lithium ion batteries employ crystalline materials which have stable electrochemical potentials and storage sites to allow lithium ion intercalation within the interstitial layers or spaces [29]. The predominant active electrode materials have been a lithiated metal oxide for the cathode (positive electrode) and a graphitic carbon as the anode (negative electrode). However, new cathodes with higher capacities and voltages and new anodes with higher capacities are being investigated to increase energy density. The potential difference of the cell will be determined by the choice of cathode and anode as shown in Figure 3.

![Figure 3](image_url)

*Figure 3. Specific capacity and voltage of lithium ion active cathode and anode materials (Reproduction for dissertation allowed by The Royal Society of Chemistry (RSC)[25]).*
The active materials are combined with a binder (e.g. polyvinylidene fluoride – PVDF) and conductive additives (e.g. carbon black, graphite, etc.) prior to being deposited onto metal foil current collectors. An example of the process at a lab scale is shown below in Figure 4.

**Figure 4.** Standard lithium ion battery electrode fabrication process at a lab scale (Original photographs taken at RIT and final electrode image reproduction for dissertation allowed by The Royal Society of Chemistry (RSC)[25]).

The electrodes are electrically insulated in the battery through a polymer separator, most often with a microporous polypropylene/polyethylene laminate, that allows for lithium ion diffusion. Historically, the majority of commercial batteries have utilized LiCoO$_2$ as the active cathode material and either graphite or mesocarbon microbeads (MCMBs) as the active anode material. The composite thicknesses can range from 75 to 200 µm on thin (12-20 µm) metal foil current collectors for typical high energy density lithium ion batteries. It is important to note that the composite thickness values are highly sensitive to the formulation, calendaring, and intended application design towards high energy density (thicker active layer) or high power density. The high power batteries being produced today typically rely on an active layer thinning strategy to increase the charge-discharge rates. This strategy presents a severe reduction in the total energy density in the battery because the relative mass of metal foil current collector increases compared to the active material. Overall, the selection of active materials is extremely important to
performance, but processing variables (e.g. active material/binder/additive concentration, deposition conditions, active layer thickness, etc.) are just as critical to achieving state-of-the-art (SOA) electrodes.

A lithium ion battery operates by movement of lithium ions from the cathode to the anode upon charge and the reversible process occurs during discharge, as shown by the schematic in Figure 5. The lithiated metal oxides and graphitic carbons are layered materials with interstitial spaces receptive to lithium ion intercalation. The active material is able to store the lithium due to the simultaneous electron transport from the current collector to reduce the lithium ion at the active material “host” site.
Figure 5. Schematic illustrating the mechanism of operation for a lithium ion battery including the movement of ions between electrodes (solid lines) and the electron transport through the complete electrical circuit (dashed lines) during charge (blue) and discharge (red) states (Reproduction for dissertation allowed by The Royal Society of Chemistry (RSC)[25]).

The intercalation process is aided by a necessary solid-electrolyte-interface (SEI) that forms on the surface of each electrode which serves a critical role, namely to passivate the electrode surface from further solvent reduction and as a selective layer to allow only lithium ions to diffuse [30]. The lithium ions are present in an electrolyte comprising a lithium salt, most often LiPF$_6$, solvated by a mixed solution of alkyl carbonates (i.e. ethylene carbonate (EC), dimethyl carbonate (DMC), etc.). The choice of electrolyte solvent is critical to forming a stable SEI due to subtle decomposition of both salt and solvent species leading to critical components like LiF and LiCO$_3$ which form the SEI [30]. The electrolyte formulation and origin of SEI components has been a major research area and is still an ongoing study for new lithium salts and solvents.
with improved ionic conductivity or temperature ranges [31, 32] The SEI composition and stability is an important factor when evaluating the safety of electrodes and the overall battery.

The battery form factor can vary depending on application and some of the more common types are coin, cylindrical, prismatic, and pouch cells. The choice of form factor will affect the size and amount of energy per cell as well as the both volumetric and gravimetric energy density due to the shape and weight of the container. One of the most ubiquitous commercial form factors is the 18650 cylindrical cell which is 18 mm in diameter and 65 millimeters in height. The data in this dissertation was taken at the lab scale in which a small area of electrodes was used. The 2032 (20 mm x 3.2 mm) coin cells were utilized in the electrochemical testing in this work, and the cells were prepared in an Argon filled glove box. The testing was performed using an Arbin BT-2000 cycler using Kelvin clips in a gravity convention oven at a constant temperature of 30°C to reduce fluctuations in data due to temperature. The majority of testing of electrodes was done versus lithium metal using 1.2M LiPF₆ EC:EMC electrolyte in a 3:7 volume ratio. Cathodes were tested using a constant current-constant voltage charging and a constant current discharge. The charging consisted of applying a constant current until the voltage reached a set limit (around 4.2-4.3V for most cathodes), and the then the voltage was held constant until the current dropped to below 10% of the previous constant current. An example of a cathode vs. lithium voltage profile is shown in Figure 6 with some important parameters noted.
Figure 6. Example charge-discharge voltage profile of a NCA cathode versus lithium metal.

The average discharge voltage and the reversible (discharge) specific capacity will determine the energy of the active material versus lithium. This data is shown in reference to specific capacity or capacity per mass of active cathode material and does not take into account other electrode components such as binder, conductive additives, and current collector. The reversible specific capacity is a commonly referenced value and is colloquially referred to as cathode capacity. The coulombic efficiency (CE) is also an important value which relates to the percentage of charge that is reversibly cycled. This value can tell how efficient the cell is and is typically lower on the first cycle due to loss of lithium and SEI formation. The electrochemical data is dependent on
the constant current rate, which is often referred to as C-rate, which can change the average voltage and discharge capacity due to internal resistance and material rate limits. C-rate and other important testing terms and formulas are summarized and defined below.

**C-rate** - C/t rates (where t is the time for a complete charge or discharge in hours)

**Specific Capacity** \[= \frac{\text{Current (mA)} \times \text{time (h)}}{\text{Active Mass (g)}} \]

**Average Discharge Voltage (V)**

**Coulombic Efficiency (CE)** \[= \frac{\text{Extraction Capacity}}{\text{Insertion Capacity}} \times 100 \]

**Gravimetric Energy Density** \[= \frac{\text{Capacity (Ah)} \times \text{Voltage (V)}}{\text{Total Cell Mass (kg)}} \]

*Specific capacity can be presented as a function of the active mass only or the entire electrode mass (including binder, additive, and current collector)*

The cathode discharge voltage profiles with changing chemistries are shown in Figure 7. The average voltage and discharge capacity is directly related the cathode chemistry. A higher voltage and capacity would provide the largest energy; however, current electrolytes become unstable above 4.5 V and must be addressed to utilize higher voltage cathodes.
When testing electrodes that are considered anodes versus lithium, the charge and discharge are reversed and the anode is acting as the cathode in the cell. Therefore, for clarity, when testing anodes versus lithium, the axes are labeled insertion and extraction capacity based on whether lithium ions are being intercalated or extracted from the anode. An example of an anode voltage profile versus lithium can be seen in Figure 8. The extraction capacity is the reversible capacity that is reported as the materials specific capacity. The average voltage plateau will affect the battery energy when paired versus a cathode. A lower anodic voltage increases the energy by increasing the overall battery potential difference. When paired versus a cathode, the capacity above 1.5V is typically not accessed and is pointed out in Figure 8.

**Figure 7.** Discharge voltage profiles of cathodes with varying chemistries.
Figure 8. Example charge-discharge voltage profile of a anode versus lithium metal.

When the cathode and anode are paired in a typical battery configuration, the resulting voltage profiles look similar to the cathode voltage profiles versus lithium. However, the voltage is lowered by the potential difference of the anode versus lithium. Figure 9a demonstrates the changing voltage profiles when pairing NCA cathode versus different active anode materials. The change in voltage directly correlates with the change in anode voltage vs. lithium as shown in Figure 9b.
Figure 9. (a) Discharge voltage profiles of NCA cathode versus varying anode chemistries. (b) Lithium extraction voltage profiles of common anodes versus lithium.

The cathode and anode capacities must be matched by areal specific capacity (Ah/cm²) in order to maximize energy and cycleability. A slightly higher anode areal loading is typically utilized to minimize the chance of lithium plating and maximize the use of cathode capacity. A capacity matching diagram of electrodes is demonstrated in Figure 10.
Figure 10. Diagram of lithium ion battery materials with capacity matching areal loadings (original diagram produced by the author).

The cathode capacity is currently significantly lower (150-180 mAh/g) than the standard graphitic anode capacity (300 mAh/g). Therefore, the anode composite has a lower areal mass loading (mg/cm$^2$) to match the cathode resulting in a thinner coating. This has an effect on energy density especially in high power designs where the electrodes are thinned to enable faster transport. In that case, the mass of the inactive metal current collector becomes a greater percentage, and reduces overall energy density. The lower cathode capacity also reduces the benefits of a higher capacity anode such as Si and Ge, because the anode layers have to be thinned to match the cathode. It is important to note that a significant increase in energy density is not found above anode capacities of 1000 mAh/g. The coulombic efficiency of the anode will also affect capacity matching where excess loss of lithium due to SEI formation, typically due to high surface area, has to be accounted for through excess cathode loading (decreasing cell energy density) or through anode pre-lithiation techniques.
**Dissertation Topics and Significance**

The focus of this dissertation is to advance the performance and thermal stability of lithium ion batteries while monitoring material impacts and identifying sustainable strategies to address end-of-life (EOL) management. A typical life cycle of a lithium ion battery is shown in Figure 11 with varying EOL management pathways. Two specific nanomaterials are being evaluated: single wall carbon nanotubes (SWCNTs) and lithium iron phosphate (LiFePO₄). SWCNTs are a next generation nanomaterial that will be researched for use in lithium ion batteries in a variety of ways to improve performance in the use phase while monitoring the environmental impact of material extraction and synthesis. LiFePO₄ is a wide-spread commercially available cathode nanomaterial for which the EOL management will be investigated.

![Lithium Ion Battery Life Cycle](image)

**Figure 11.** Life cycle of lithium ion battery with EOL management options (Original figure produced by the author).
The first topic investigates the beginning of life (cradle) environmental impact of SWCNTs by measuring the energy of SWCNT production through laser vaporization and comparing to potential gains in electrochemical performance. SWCNTs can be envisioned as a rolled up sheet of graphite that is one atom in thickness, 0.5-3 nm in diameter, and can be many microns in length. They are well known for their superlative electronic, optical, mechanical, and thermal properties. SWCNTs have been shown to improve the performance of lithium ion battery electrodes; however, the energy to produce and purify SWCNTs has been measured to be high compared to other battery materials and should be monitored to understand the environmental impact. A variety of SWCNT production methods exist, and previous studies on production energy have focused on CVD processes[33]. The SWCNTs used in this dissertation were produced through laser vaporization; therefore the embodied energy of SWCNTs produced by laser vaporization was measured for the first time in topic I[34].

The second topic focuses on the use phase where SWCNTs are being incorporated as novel conductive additives and current collector supports to improve the performance and thermal stability of lithium ion batteries. SWCNTs can be incorporated into lithium ion battery electrodes as a conductive additive, replacement to the current metal collector, and as a lithium ion storage material on the anode. Most of the initial research on SWCNTs in lithium ion batteries focused on the use as a free-standing anode because of a high theoretical capacity (>1116 mAh/g) where the SWCNTs would be both the active material as well as the current collector[35]. However, a sloping voltage profile and a high first cycle loss, due to the high surface area causing a large amount of SEI, has made the use as an anode storage material impractical[25]. Therefore, the research has recently focused on taking advantage of the highly
conductive and light-weight material to improve rate capability and reduce mass thus improving energy density. Topic II will discuss use of SWCNTs as a conductive additive and as a free-standing support with next generation anode nanomaterials such as Si and Ge and the resulting effect on electrochemical performance and safety of electrodes.

The last topic investigates the EOL management of a commercially available nanomaterial: LiFePO₄. Batteries containing LiFePO₄ are already entering the waste stream, and a proper EOL pathway is unknown due the lower value of elements within the cathode. An ideal EOL pathway would be the recovery and treatment of the LiFePO₄ material to regain electrochemical performance without the need to recycle to the elements. This new pathway is defined as *refunctionalization*, and is investigated to provide a new avenue for cathode materials at EOL. Commercial cells containing LiFePO₄ were cycled to investigate capacity fade mechanisms. The cells were dismantled before and after EOL to obtain a bill of materials (BOM), and enable separation of the battery components. Refunctionalization of the LiFePO₄ cathode was investigated by electrochemical and chemical lithiation to regain its original performance (e.g. crystallinity and capacity). The environmental impact of the refunctionalization process was determined by calculating the embodied energy of the process and comparing to LiFePO₄ materials produced from virgin and recycled materials.
In summary, the work will be split into three main sections which will address the dissertation topics discussed above. The objectives for each section are as follows:

1. Environmental Impacts of Nanomaterials for Li⁺ Batteries
   - Determine the embodied energy of purified SWCNTs produced by laser vaporization that were utilized in all these studies to establish a life cycle inventory.
   - Compare to other synthesis methods and isolate potential areas for embodied energy reduction

2. Performance and Safety of Li⁺ Batteries Using Nanomaterials
   - Incorporate SWCNTs into electrode composites as conductive additives and test effect on lithium ion battery performance (e.g. capacity, rate capability, energy density, and coulombic efficiency).
   - Investigate the safety of electrode composites with SWCNT conductive additives using differential scanning calorimetry.
   - Use SWCNTs to increase energy density of Li⁺ batteries by increasing the thickness of cathode composites or using as free-standing supports for standard electrodes.
   - Test the safety of next generation free-standing SWCNT anode composites with Si and/or Ge.
3. Commercial Battery Health Monitoring and End-of-Life

- Disassemble commercial 18650s with nanomaterial cathode, LiFePO$_4$, and obtain a bill of materials.

- Investigate refunctionalization treatments to recover the performance of the electrode or LiFePO$_4$ material through removal of SEI layer or dissolution of cathode coating to recover LiFePO$_4$.

- Compare embodied energy of LiFePO$_4$ synthesized from virgin or recycled materials to the refunctionalized LiFePO$_4$ embodied energy to determine environmental impact.
TOPIC I. CRADLE - ENVIRONMENTAL IMPACTS OF NANOMATERIAL PRODUCTION

Overview

This section discusses the environmental impact of SWCNTs through the monitoring of the embodied energy of the synthesis and purification process. Previous work has looked at SWCNT production through arc and chemical vapor deposition methods, but no work has accounted for the embodied energy of SWCNTs through the laser vaporization process, and taken a through look at purification energy [33, 36, 37]. High purity laser vaporization SWCNTs are desirable for the present work due to their high quality, which motivated the analysis of the embodied energy of this synthesis process. Direct energy measurements were made at the lab scale to provide an accurate characterization of the SWCNT synthesis process within a life cycle framework, and determine potential areas for energy savings. The embodied energy work was published in a conference proceeding:

Chapter 1. Embodied Energy of SWCNT Production

i. Introduction

Due to their unique electrical, thermal, and mechanical properties, single wall carbon nanotubes (SWCNTs) have attracted considerable interest for use in a number of applications such as lithium ion batteries, fuel cells, and conductive wiring[38]. However, the energy required to synthesize and purify SWCNTs in the manufacturing phase must be considered in order to fully realize the benefits in the use phase, and gain a life-cycle understanding[39]. The laser vaporization process consists of production of the raw SWCNT material, refluxing in acid to reduce metal content, and a final burn to remove amorphous carbon content. Each step introduces electrical and material inputs that can be adjusted to affect the yield and material properties. Various manufacturing techniques exist for SWCNTs and each result in materials of differing purity (mass fraction of SWCNTs), chirality, diameter, and length distributions. While manufacturing energies for some of these other SWCNT production techniques have been reported, a systematic analysis of the laser vaporization processes energy consumption from each step is lacking, and can be used to address and reduce the areas of greatest energy consumption.

Previous reports have estimated the energy required to manufacture and purify SWCNTs in a range of $1.6\times10^5 - 8.1\times10^7$ MJ/kg for arc ablation, chemical vapor deposition, and the HiPCo processes and it is unclear whether upstream embodied energy from electricity production in accounted for [33, 36, 37, 40]. Many of the literature reports are based on data accumulated from indirect sources – such as data reported from manufacturing companies or other literature studies -- and do not account for differences in material properties. These variations may be extremely important to the performance of the final product, but are typically not characterized
in existing life-cycle energy studies. For example, a low-yield synthesis technique requires more energy on a pure-mass basis – both because of high waste rates and because of the additional energy-intensive purification processes required. While no synthesis method typically produces more than 30% by weight SWCNTs, laser vaporization generally results in the highest purity SWCNT material[41]. The synthesis, purification, and purity assessment of laser produced SWCNTs have been well studied in the literature, but have yet to be compared with the resulting energy of production[42, 43]. Therefore, the absence of process energy consumption data regarding laser vaporization represents a significant knowledge gap that this research seeks to fill.

ii. Methods

SWCNT Laser Vaporization Production

The SWCNT materials were synthesized by laser vaporization using a pulsed Nd-YAG laser as described previously[41]. The reaction furnace temperature was maintained at 1150°C, with a chamber pressure of 760 torr under 200 sccm flowing Ar. The target was pressed at 2,500 psi and contained 94% w/w graphite (1-2 µm), 3% w/w Ni (submicron), and 3% w/w Co (1-2 µm). The raw SWCNT soot was purified by acid reflux at 120°C for 12 hours as reported previously[41]. The reflux solution was filtered over a 1µm PTFE membrane filter with excess distilled H₂O to form a SWCNT paper. The acid filtrate was discarded and subsequent washes (3x) with acetone and distilled H₂O removed functionalized carbon impurities until the filtrate was clear. The resulting paper from acid-reflux was ultimately purified using thermal oxidation profiling (TOP) to determine the appropriate time and temperature conditions[41]. The purity of the resulting SWCNT paper after acid reflux and thermal oxidation at varying temperatures was
determined using an optical absorption purity assessment established in previous work [41]. To assess the purity, a 3.13 ug/mL dispersion of SWCNTs in the organic solvent N, N, Dimethylacetamide (DMA) was formed using ultrasonication. It is well known that the absorption peaks correlate directly with the electronic transitions of the chiralities present within a SWCNT sample [44]. This purity method uses a ratio of the secondary semi-conducting transition to the first metallic transition to establish purity based upon a “100%” pure reference sample which is established as a “100% sample.

An overall process flow diagram is presented in Figure 12 with the electricity and material flows. In the synthesis stage, a metal-catalyst impregnated graphite target is vaporized with a high-intensity laser in a high temperature furnace. The resultant carbon vapor condenses as it cools in the furnace chamber, nucleating at the site of the metal catalyst particles to form raw SWCNT soot.

The soot can be purified through an acid reflux that dissolves the metal catalyst and acetone rinses to remove functionalized carbon materials which result in the formation of a solid paper on the surface of the filter membrane. The paper is then thermally oxidized in a furnace to burn of any remaining amorphous carbons to create a purified SWCNT paper. Most of the input materials promptly become waste, although unused graphite/metal target material is recycled. The energy considerations of the laser vaporization process are from the electrical energy of the single zone furnace, the laser during use, the material inputs of the target, and inert gas flow. The acid reflux process consumes hydrochloric and nitric acid, deionized water, and requires electricity from the hotplate. The filtration step uses electrical energy when pumping out the
consumed deionized water and acetone from the rinsing process. The resulting filtered paper then requires electrical energy from a muffle furnace to burn off any amorphous carbon contents, and produces CO$_2$ as a bi-product. The inputs and outputs are shown in Figure 12 with the process in the middle of the diagram, and the final waste locations shown in the circles at the top of the figure (where POTW is publicly owned treatment works).

**Figure 12.** Process diagram depicting material and energy flows in production of a purified SWCNT paper. At the laboratory scale, most material and energy inputs become waste (Reproduction for dissertation allowed by IEEE [45]).
Goal and Scope

The goal of this analysis is to monitor the electrical energy and chemicals consumed to produce 1kg of purified laser vaporization produced SWCNTs and calculate the cumulative energy demand (CED) using a life cycle framework. The cumulative energy demand (CED) was modeled in SimaPro (Pre, The Netherlands) was applied to determine the electric energy and material environmental impacts of SWCNT production and purification through laser vaporization using ecoinvent database. CED includes all energy inputs across the life cycle of the materials, including both direct process electricity, as well as energy required to produce electricity and other raw materials. The scope of this analysis is from the starting materials (graphite and metal catalyst) to the final purified product, and only accounts for the material and energy consumed. Waste streams, emissions, and any recycled materials or chemicals are not included in this analysis. The CED is modeled using the materials available in Ecoinvent and doesn’t account for the purification or altering of specialty starting materials (e.g. micron sized metal catalyst). The energy calculations were made assuming an eight hour run with a production rate of 100 mg/hr which is an average value for the laboratory scale laser process. The typical purity of the material is around 30% which would make for 240mg of pure SWCNTs produced per 8 hour workday. The reflux energy was calculated using a time of 12 hours. The purification energy was calculated assuming purification of SWCNT produced over one day. Direct measurement of the electrical energy consumption in a laboratory-scale laser vaporization process was performed. Energy and material inputs along with the resultant waste stream data were obtained from existing laboratory-scale production processes in the raw, reflux, and final purification processes.
The electrical energy of the hotplate, vacuum pump, and muffle furnace was obtained using a plug-in power meter watts up? PRO. The electrical energy of the single-zone furnace and Nd-YAG laser were measured using Extech datalogging AC/DC Power Clamp-on Meter Model 382065/382068. Time and temperature of final thermal oxidation purification step was compared with purity established through optical absorption alongside the resulting change in energy use.

**Energy and Material Inventory**

The electrical inputs and the resulting measured electrical energy inventory are shown in Table 1. The largest energy consumption occurs during the synthesis process where the laser and high temperature furnace are running for the entire day with a production rate of 100 mg/hr. The electrical energy for the synthesis and purification process added up to 113.8 MWh/kg which in the range of the electrical energy previously reported from 40-280 MWh/kg[33].

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy Inputs (Electricity)</th>
<th>Electrical Energy Consumed (MWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Vaporization</td>
<td>1 Zone Furnace</td>
<td>53.1</td>
</tr>
<tr>
<td></td>
<td>Nd-YAG Laser</td>
<td>38.7</td>
</tr>
<tr>
<td>Reflux</td>
<td>Hotplate</td>
<td>19.8</td>
</tr>
<tr>
<td>Filtration</td>
<td>Vacuum Pump</td>
<td>0.8</td>
</tr>
<tr>
<td>Thermal Oxidation</td>
<td>Muffle Furnace</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>113.8</td>
</tr>
</tbody>
</table>

**Table 1.** Inventory of measured electrical energy inputs
The material inputs were recorded during the production, reflux, and thermal oxidation steps. The tabulated masses of input inventory used are given in Table 2.

<table>
<thead>
<tr>
<th>Process</th>
<th>Process Inputs</th>
<th>Mass Consumed (kg)/kg pure SWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Vaporization</td>
<td>Graphite</td>
<td>3.133</td>
</tr>
<tr>
<td></td>
<td>Cobalt</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td>0.7125</td>
</tr>
<tr>
<td>Acid Reflux</td>
<td>HNO₃</td>
<td>1.258</td>
</tr>
<tr>
<td></td>
<td>HCL</td>
<td>0.472</td>
</tr>
<tr>
<td></td>
<td>DI Water</td>
<td>3.3333</td>
</tr>
<tr>
<td>Filtration</td>
<td>Acetone</td>
<td>0.658</td>
</tr>
<tr>
<td></td>
<td>DI Water</td>
<td>1.667</td>
</tr>
</tbody>
</table>

**Table 2.** Inventory of material Inputs
The ecoinvent data sources for the energy and material inputs modeled in Simapro are listed in Table 3 for each process in the laser vaporization production and purification of SWCNTs.

<table>
<thead>
<tr>
<th>Process</th>
<th>Inputs</th>
<th>EcoInvent Data Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Vaporization</td>
<td>1 Zone Furnace Energy</td>
<td>U.S. Medium Voltage at Grid</td>
</tr>
<tr>
<td></td>
<td>Nd-YAG Laser Energy</td>
<td>U.S. Medium Voltage at Grid</td>
</tr>
<tr>
<td></td>
<td>Graphite</td>
<td>Graphite, at plant/RER U</td>
</tr>
<tr>
<td></td>
<td>Cobalt</td>
<td>Cobalt, at plant/GLO U</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
<td>Nickel, 99.5%, at plant/GLO U</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td>Argon, liquid, at plant/RER U</td>
</tr>
<tr>
<td>Reflux</td>
<td>Hotplate Energy</td>
<td>U.S. Medium Voltage at Grid</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>Nitric acid, 50% in H₂O, at plant/RER U</td>
</tr>
<tr>
<td></td>
<td>HCL</td>
<td>HCL, 30% in H₂O, at plant/RER U</td>
</tr>
<tr>
<td></td>
<td>DI Water</td>
<td>Water, deionised, at plant/CH U</td>
</tr>
<tr>
<td>Filtration</td>
<td>Vacuum Pump Energy</td>
<td>U.S. Medium Voltage at Grid</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>Acetone, liquid, at plant/RER U</td>
</tr>
<tr>
<td></td>
<td>DI Water</td>
<td>Water, deionised, at plant/CH U</td>
</tr>
<tr>
<td>Thermal Oxidation</td>
<td>Muffle Furnace Energy</td>
<td>U.S. Medium Voltage at Grid</td>
</tr>
</tbody>
</table>

**Table 3.** Ecoinvent data sources for energy and material inputs.
iii. Results and Discussion

Impact Assessment

The CED impact was calculated for each energy and material input and are summarized along with the ecoinvent data sources in Table 4. The results show a very small embodied energy contribution from the materials and chemicals compared to the electrical energy consumed where electrical energy accounts for 99.98% of the total CED of 1.44E+06 MJ/kg.

<table>
<thead>
<tr>
<th>Process</th>
<th>Inputs</th>
<th>CED (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Vaporization</td>
<td>1 Zone Furnace Energy</td>
<td>6.80E+05</td>
</tr>
<tr>
<td></td>
<td>Nd-YAG Laser Energy</td>
<td>4.96E+05</td>
</tr>
<tr>
<td></td>
<td>Graphite</td>
<td>1.67E+00</td>
</tr>
<tr>
<td></td>
<td>Cobalt</td>
<td>1.28E+01</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
<td>1.87E+01</td>
</tr>
<tr>
<td></td>
<td>Argon</td>
<td>4.89E+00</td>
</tr>
<tr>
<td></td>
<td>Laser Vaporization Total</td>
<td>1.18E+06</td>
</tr>
<tr>
<td>Reflux</td>
<td>Hotplate Energy</td>
<td>2.54E+05</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>1.68E+01</td>
</tr>
<tr>
<td></td>
<td>HCL</td>
<td>8.27E+00</td>
</tr>
<tr>
<td></td>
<td>DI Water</td>
<td>6.35E-02</td>
</tr>
<tr>
<td></td>
<td>Reflux Total</td>
<td>2.54E+05</td>
</tr>
<tr>
<td>Filtration</td>
<td>Vacuum Pump Energy</td>
<td>1.79E+01</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>4.43E+01</td>
</tr>
<tr>
<td></td>
<td>DI Water</td>
<td>3.18E-02</td>
</tr>
<tr>
<td></td>
<td>Filtration Total</td>
<td>6.22E+01</td>
</tr>
<tr>
<td>Thermal Oxidation</td>
<td>Muffle Furnace Energy</td>
<td>1.02E+04</td>
</tr>
<tr>
<td>Total CED</td>
<td></td>
<td>1.44E+06</td>
</tr>
</tbody>
</table>

Table 4. Cumulative Energy Demand (CED) impact assessment data
The low yield of SWCNTs produced contributes to the high embodied energy per kg of SWCNTs produced. The SWCNT synthesis process accounts for 80% of the total embodied energy as demonstrated in Figure 13 where the synthesis furnace is the single largest energy consumer.

![Figure 13. CED of production and purification processes.](image)
Interpretation

The total CED of 1.44E+06 is in the range previously published for other SWCNT synthesis methods of 1.6E05 – 8.1E07 MJ/kg [33, 36, 37, 40]. Also, it is unclear whether the previous studies accounted for upstream energy consumption which would increase the CED threefold. The measurements for this work were taken at the lab scale and slight process improvement could put the embodied energy below that of methods. This is in contrast to the predictions within the literature that the process wasn’t scalable enough and the energy consumption would be significantly high [33, 36, 37]. Even at the laboratory scale, it shown that laser vaporization consumes a low amount of energy, compared to other SWCNT production methods, due to its high initial soot purity and ease of purification. The purity of the SWCNT materials in previous studies is unclear and could affect the embodied energy calculated. For example, if the purity of the material in the previous work was only 60% w/w than the embodied energy range for the previous SWCNTs studied would increase to 2.65E+05 MJ/kg to 1.35E+08 MJ/kg where laser vaporization is comparable to the lowest SWCNT embodied energy methods. This gives the potential that with a scaled up process that laser vaporization could become a commercial option to produce carbon nanotubes. Laser vaporization is a useful production method because of the many variables that can be changed in order to get different chiralities of SWCNT material. The carrier gas can be changed to produce larger or smaller diameter SWCNTs[43]. Higher pressures can produce higher purities of materials, and laser power can be increased to increase yield.
Often purification protocols and standards are performed without a direct understanding of the resulting purity of the material, and the efficiency that the purification is performed. The raw SWCNT material produced is approximately 30% by weight pure SWCNTs, and efforts should be made during purification to obtain the highest purity possible without sacrificing any material. The purity measured through optical absorption is shown below in Figure 14 at varying temperatures.

![Graph showing SWCNT purity and total mass loss](image)

**Figure 14.** SWCNT purity and total mass loss of the paper from thermal oxidation for ten minutes is plotted versus temperature of the oxidation. The dotted lines are provided as guide to the eye, and should not be considered exact trends (Reproduction for dissertation allowed by IEEE[45]).
The highest purity obtained is at 600°C for a ten minute isothermal condition in the muffle furnace after the temperature was reached. The purity of the material levels out after 600°C, but increased mass is lost with increasing temperature. In many applications, and that of this dissertation, it was the goal to obtain the highest purity while retaining the highest mass of pure SWCNTs possible. The 60% mass loss is typical for this step of the purification since 30% is pure SWCNTs and there are some intercalated acids from the reflux process that burn off. The electrical energy consumed by the muffle furnace was also measured and ranged from 0.3 MWh/kg to 1.7 MWh/kg which is fairly insignificant compared to the laser and single-zone furnace as can be seen in Table I, which uses the energy consumed at 600°C. This is also assuming that only one day worth of material is purified at a time, but the energy would be even lower if a larger amount of material is purified at once. The embodied energy/kg SWCNT material can be greatly improved if a process calls for a material of less purity. If raw material is acceptable, the MJ/kg could improve over three times. The energy needed to produce a particular quantity is directly correlated to the amount of amorphous carbon and metallic content is allowable for a certain process.

The largest contributors to the SWCNT embodied energy through laser vaporization are from the synthesis laser and furnace. Increases in efficiency and production rate would significantly reduce the embodied energy of the process. The use of a more efficient or solar furnaces are some possibilities to reduce the embodied energy. A more efficient laser would also reduce the energy consumption, and higher yields may be possible with larger laser spot sizes.
Summary and Acknowledgements

The embodied energy of laser vaporization of SWCNTs was found through direct measurement of electrical energy and material usage and the CED was calculated. The total energy found for production and purification was found to be at the low end of the range found in previous reports for production methods. The high purity and known purification assessment method are advantages for the laser vaporization process. The next topic will demonstrate the improvement in lithium ion battery performance that can be realized with the use of these high purity materials. However, the embodied energy of SWCNTs is still orders of magnitude higher than the battery materials that are being replaced. The effect of the incorporation of high embodied energy materials on the overall life cycle embodied energy of lithium ion battery devices is still not well understood. Previous studies have estimated that only 2% of electric vehicle life cycle energy is due to the battery materials embodied energy, where the majority of the energy is consumed in the use phase[46]. Therefore, use phase improvement may outweigh the impact of incorporating high embodied energy materials. However, the studies are complicated based on functional unit and cycle life assumptions, and the actual use phase for the CNTs is unclear. A complete analysis comparing the embodied energy impacts to the use phase improvements was not pursued in this work, but based on progress in the dissertation it will be in the future. Use phase energy density improvement is significant for electric vehicles where the battery has a large mass such as the Tesla model S which contains 7000 - 18650 cells and weighs 1300 lbs[47]. Therefore, a doubling of energy density can lead to a reduction of the pack mass by half while storing the same amount of energy. The weight savings can improve fuel economy and also requires less mechanical supports in the vehicle. A pack with the same mass could be used as well that has double the energy storage capacity and vehicle driving range. Also, it should be
noted that SWCNT production is still at its infancy and many studies are at the lab scale. Significant gains are expected with scale and efficiency improvements which has been the case for other emerging technologies. Higher energy efficiency may be gained through increased production rate with scale, more efficient furnaces, and the recovery and recycling of gases and target materials. Previous work has shown that the electricity use per MHz in fabricating desktop microprocessors has decreased from 0.208 KWh/MHz to 0.001 KWh/MHz from 1995-2006[48]. Thus an order of magnitude decrease has been realized for other emerging technologies and SWCNT production is projected to follow a similar trend. Embodied energy of materials and cost can also be correlated, and significant reductions in the cost of multi-wall carbon nanotubes (MWCNTs) have already been realized. The cost of MWCNTs has decreased from $45,000/kg to 100/kg over the past ten years[49]. Also, new SWCNT production techniques should arise with better understanding of growth mechanisms, and recent work could lead to direct chemical growth of SWCNTs of higher purity thus reducing energy consumption and improving purity[50]. Therefore, significant reduction in SWCNT production embodied energy is expected in upcoming years. The author would like to acknowledge Christopher Schauerman for his assistance in electricity measurements, the SWCNT production, and creation of the purification diagram.
TOPIC II. USE PHASE - PERFORMANCE AND THERMAL STABILITY OF LITHIUM ION BATTERIES

Overview

This topic discusses improving the use phase performance of lithium ion batteries by incorporating SWCNTs into various electrode designs. The application of SWCNTs in lithium ion batteries is demonstrated to have the ability to improve power, energy, and thermal stability. The first two chapters involve a near-term application of SWCNTs as a conductive additive replacement to traditional amorphous carbon additives at a low weight percentage in both anode and cathode standard composites. A proper slurry preparation and SWCNT dispersion method was developed involving alternating sonication and planetary centrifugation applying knowledge of SWCNT dispersions in organic solvents.[51] This technique enabled the high purity SWCNTs to be uniformly distributed in the composite in order to wrap active particles and creating long range connectivity. The thermal stability of the electrodes was also monitored using differential scanning calorimetry (DSC) to determine the exothermic energy released upon overcharge which relates to the ultimate safety of the electrodes upon thermal runaway.

The remaining chapters discuss increasing battery energy density through electrode engineering by taking advantage of the lightweight SWCNTs unique properties. The first chapter discusses increasing electrode loading and thickness on metal current collectors. If the thickness or loading of the composite is increased, the relative mass of the inactive current collector is decreased thus increasing overall electrode energy density. It is predicted that SWCNT conductive additives are necessary at higher composite loadings to achieve the desired capacity
at typical charge-discharge rates by enabling higher conductivity through the composite. The last sections discuss using CNTs as a current collector replacement to support electrode materials. A larger increase in battery energy density (5-30%) can be realized by replacing the heavy metal current collectors with CNTs, especially in the case of copper. First, traditional cathode and anode composites were coated onto commercially available and mechanically robust CNT papers. The impact of proper purification of the commercial CNT paper was studied to determine the effect on electrochemical performance. Lastly, a combination of high capacity Si and Ge materials with CNT supports were tested to further increase electrode capacity. The thermal stability of these next-generation electrodes was tested through DSC to test the implications on battery thermal safety.

This work resulted in two journal publications and a conference proceeding:


Chapter 2. SWCNT Cathode Additives

i. Introduction

The higher energy and power density of lithium-ion (Li\(^+\)) batteries over other rechargeable battery chemistries have made them the preferred energy storage for portable devices, and the prevalent technology to enable electrification of vehicles [20]. The electrochemical performance of Li\(^+\) batteries is largely controlled by the choice of cathode chemistry which governs the output potential difference range and limits the capacity matching with typical anode materials due to a lower intrinsic capacity. The most common cathode structures used today, lithium metal oxides (LiMO\(_2\)), where M is primarily Co and/or Ni, are one type of high energy density cathodes, but are prone to lower power densities (above 2C rates), and thermal instability upon overcharge which causes safety concerns [52, 53].

Strategies to improve both the thermal stability and power capabilities of LiMO\(_2\) cathodes have primarily focused on modification of particle size or surface coatings [54, 55]. Power density has been shown to be improved by adjusting conductive additive type, morphology, and loading levels [56], but the effect of a high thermal conductivity additive material on the safety of cathode composites has yet to be investigated. Conductive additives are necessary in cathode composites to provide sufficient electronic conductivity between the active cathode particles and the metal foil current collector [57]. Typical conductive additives (e.g. carbon black or graphite powders) are employed at sufficient weight loadings to form an electrical percolation network (the concentration in a composite that sustains long range connectivity or contiguous pathways for electrons to move), and to balance sufficient electrode conductivity with active mass loading.
A significant development would be improved electrical and thermal properties for the composite electrode at lower weight loadings. Safety of the Li\(^+\) battery system is proposed to be improved if the heat dissipation rate is higher than that of the heat produced which will be affected by the thermal conductivity of the electrodes as well as the cell design [58].

Carbon nanotubes (CNTs) are a promising candidate as conductive additive materials to address both limitations of LiMO\(_2\) cathode composites based upon several advantages when compared to traditional carbon additives: (1) high aspect ratio and flexibility to entangle cathode particles which can prevent active particle separation with extended cycling, (2) high theoretical electrical conductivity exceeding copper, (3) large thermal conductivity of single wall CNTs (3500 W/m\(\cdot\)K) surpassing graphite (~300 W/m\(\cdot\)K) and carbon black (<1 W/m\(\cdot\)K) by more than an order of magnitude [59, 60]. To date, multi-walled CNTs have been predominantly investigated in cathodes; showing ~10% improvement in the reversible capacity of the electrodes up to an equivalent of a 3C rate for LiCoO\(_2\) compared to carbon black counterparts [61, 62]. Single wall CNTs (SWCNTs) have only recently been investigated as a conductive additive in Li-ion battery cathode composites [63, 64]. The use of SWCNTs as a conductive additive in a typical LiCoO\(_2\) cathode coating found that 0.5% commercially prepared HiPco SWCNTs (CNI/Unidym previously, now through NanoIntegris) can effectively replace 10% carbon black and realize nearly equivalent electrode conductivity, cell impedance, and rate capability [63]. However, the potential safety improvement from using a SWCNT conductive additive with high thermal conductivity on the stability of delithiated LiMO\(_2\) cathodes has yet to be examined. It should also be noted that the SWCNT production method, purity, and dispersion in the slurry and
resulting composite could have a significant impact on the resulting electrochemical performance of the composite, and warrants additional study.

**ii. Methods**

Cathode slurries were prepared by combining the electrode materials with N-Methyl-2-pyrrolidone (NMP) and mixing in a THINKY ARE-310 planetary centrifugal mixer at 2000 rpm. The slurries were coated onto an aluminum foil (18 μm, Fukuda) using a RK Control Coater 101 with adjustable spreading blade applicator, and dried subsequently at 80°C for 1 hour. The control cathode slurry incorporating Super C65 (TIMCAL) was mixed at a mass ratio of 92 wt% LiNi$_{0.8}$Co$_{0.2}$O$_2$ (Merck), 4 wt% KYNAR Powerflex polyvinylidene fluoride (PVDF), and 4 wt% Super C65 in NMP. Cathode slurries integrating SWCNTs as a conductive additive replacement were mixed at a mass ratio of 95 wt% LiNi$_{0.8}$Co$_{0.2}$O$_2$, 4 wt% PVDF, and 1 wt% SWCNTs in NMP. The SWCNT material used in the current study was produced through laser vaporization and purified to the equivalent of the “100%” reference standard as in previous work [41, 42]. The slurry containing SWCNTs was formed by alternating bath ultrasonication (38.5-40.5 Hz at 40°C) and planetary centrifugal mixing of the SWCNTs in double the NMP volume with PVDF, before centrifugal mixing, to improve the dispersion and final mixing with LiNi$_{0.8}$Co$_{0.2}$O$_2$. In order to compare the composites, the loading and thickness were matched by coating the 1 wt% SWCNT additive slurry at a adjustable blade height until a coating of equal loading and thickness to that of the 4 wt% super C65 additive composite was obtained. Each composite electrode was then vacuum dried at 100°C and compressed using a chrome coated roller (MTI) with a 50 μm gap between rollers which resulted in a composite thickness of 40 ± 5 μm. Thickness measurements were made on cathode cross-sections using a Nikon optical microscope.
with a Nomarski prism at 200x magnification. The total composite mass loading was 8.5 mg cm\(^{-2}\) and the electrode density was 2.125 g cm\(^{-3}\) for both composites.

The electrodes were galvanostatically cycled using an Arbin BT-2000 at 25°C in a LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\) vs. Li/Li\(^+\) cell using a lithium metal foil in a 2032 coin cell configuration with a Celgard 2325 separator. The electrolyte was 1.2M LiPF\(_6\) in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a ratio of 3:7 by volume, respectively. The analysis of capacity as a function of rate was performed between 3.0 - 4.25V vs. (Li/Li\(^+\))/V. A specific capacity of 185 mAh g\(^{-1}\) was assumed for LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\) [65], to establish constant current C/t rates (where t is the time for a complete charge or discharge in hours), and the cells were discharged at C/10 (0.164 mA cm\(^{-2}\)), 2C (3.3 mA cm\(^{-2}\)), 5C (8.2 mA cm\(^{-2}\)), and 10C (16.4 mA cm\(^{-2}\)). The charge rate was a C/10 for the initial cycles that were discharged at a C/10, and was C/5 for the remaining discharge rates.

Scanning electron microscopy was performed using a field emission Hitachi S-900 microscope at 2kV. Electrical conductivity (S m\(^{-1}\)) was measured on Van der Pauw geometry electrodes after coating of slurries onto a non-conductive kapton substrate. Measurements were performed via a 4-point probe using a National Instruments (NI PXIe-1062Q) source measure unit in conjunction with a National Instruments (NITB-2606) matrix terminal block. Cross-sectional thicknesses of the anodes were measured using the Nikon optical microscope.

Differential Scanning Calorimetry (DSC) measurements were performed using a TA Q100 DSC, and heating at a rate of 10°C/min under a nitrogen purge. Samples were prepared by charging
half cells to 4.3V vs. (Li/Li^+)/V after a complete charge-discharge cycle and a constant output potential difference float charge at 4.3V for 12 hours to delithiate the LiNi_{0.8}Co_{0.2}O_{2}. The electrodes were removed from the coin cells in an argon-filled glove box, and sealed in an aluminum DSC pan with an additional 5 µL of new electrolyte before removing from glove box for measurement. The specific exothermic energy released (J kg^{-1}) was calculated by integrating under the main peak from 175 – 275°C based upon the heat flow data normalized to the active cathode material mass. Triplicate samples were analyzed to account for any slight variations in coating, electrolyte uptake, and sample preparation.

iii. Results and Discussion
SWCNTs were utilized as a conductive additive replacement at a weight loading of 1% in a LiNi_{0.8}Co_{0.2}O_{2} cathode composite and compared to a control with a carbon black additive (Super C65) at a weight loading of 4%. In contrast to the previous SWCNT conductive additive work [63], high purity laser vaporization SWCNTs were utilized in the cathode slurry using ultrasonication techniques to obtain a uniform dispersion of SWCNTs throughout the resulting composite. Characterization of the composite electrode’s electrochemical performance (i.e. capacity and rate capability) is measured to substantiate their efficacy prior to testing the effect of heat generation from delithiated cathodes using DSC. The prospect for SWCNTs to serve as conductive additives in LiMO_{2} composite cathodes and improve both power capability and thermal stability will be examined. The thickness of the composites and morphological differences between the two conductive additives are shown in the cross-section optical and SEM images in Figure 15. The thicknesses of the composites were strictly controlled to obtain average thicknesses of 40 µm for both composites with slight variations of ±5 µm. The
LiNi$_{0.8}$Co$_{0.2}$O$_2$ particles are observed in the SEM image in Figure 15a to be well coated by Super C65 carbon additive particles of slightly smaller particle size. In comparison, the cathode particles in Figure 15b show that the high purity SWCNTs are also effectively dispersed in and throughout the entire composite in small bundles, but provide a longer range interconnected nanomaterial network with the high aspect ratio SWCNTs. The electrical conductivity for the control coating using 4% Super C65 was measured to be 10.9 S/m, whereas when 1% SWCNTs are used as the conductive additive, the conductivity is increased by over an order of magnitude to 309 S/m. Therefore, the improved percolation network with SWCNTs achieves higher composite conductivity at dramatically lower additive concentration (1% w/w), enabling a higher percent of active cathode material to be used in the electrode.
Figure 15. Cross-sectional optical images of a LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode electrode with (a) 4% super C65 conductive carbon additive and (b) 1% SWCNT conductive additive. SEM images of a LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode electrode with (c) 4% super C65 conductive carbon additive and (d) 1% SWCNT conductive additive (Reproduction for dissertation allowed by Elsevier [66]).
The electrochemical performance of both cathodes cycled at an equivalent C/10 charge-discharge rate is shown in Figure 16a. The measured discharge specific capacities for the active LiNi$_{0.8}$Co$_{0.2}$O$_2$ is similar in both cases, equal to 185-188 mAh/g. The cathode incorporating 1% SWCNTs has a slightly higher 1$^{st}$ cycle discharge capacity and similar charge capacity than the control cathode composite with 4% Super C65 as a conductive additive. This results in a higher coulombic efficiency obtained for the 1% SWCNT equal to 88% compared to 87% using 4% Super C65. This increase in columbic efficiency is attributed to the improved percolation network formed by the SWCNTs, resulting in effective charge transport between the active materials.
Figure 16. (a) Comparison of 1st cycle charge-discharge voltage profiles of control composite with 4% super C65 conductive additive (dashed line) and 1% SWCNT conductive additive (solid line) at a c-rate of C/10 (0.165 mA/cm²). (b) Comparison of discharge voltage profiles at 2C (3.3 mA/cm²), 5C (8.2 mA/cm²), and 10C (16.4 mA/cm²) (results are best case scenario) (Reproduction for dissertation allowed by Elsevier [66]).
These results indicate that, at low weight loading and higher voltage range (than in an anode material), the SWCNTs are acting as a conductive additive and not reducing the coulombic efficiency from lithium storage or excessive solid electrolyte interface (SEI) formation [35]. Although the active material specific capacity is nearly the same at the low c-rates, the energy density and electrode composite capacity (normalized to mass of active material, PVDF, and conductive carbon additive) is improved by use of SWCNTs due to the lower conductive carbon mass loading. Calculation of the electrode composite specific capacity shows an increase from 179 mAh/g to 186 mAh/g is achieved through replacement of the 4% Super C65 with 1% SWCNT. The low weight loading of SWCNTs is capable of equivalent percolation, due to their intrinsic structure and electrical conductivity, and increases electrode capacity equivalent to the relative increase in active material substitution.

The similar active material capacity for LiNi_{0.8}Co_{0.2}O_2 between conductive additive materials at a lower rate (C/10) is expected as 4% Super C65 should provide sufficient electrical conductivity at the low current to achieve the expected reversible capacity. Replacing the traditional conductive carbon with SWCNTs is proposed to significantly improve the power capabilities of a high energy cathode even at a lower percentage loading due to the increase in intrinsic conductivity and improved composite percolation network [67]. Discharge rates of 2C, 5C, and 10C were tested to determine the effect of SWCNT additives on high rate electrochemical performance and results are shown in Figure 16b. At a 2C and 5C rate, the cathode incorporating SWCNTs retains a consistently higher capacity with triple the discharge capacity at a 10C rate compared to the control. In addition, the average discharge voltage is maintained at a higher value for the 1% SWCNT conductive additive electrode, which translates into an
increased cathode energy density at the higher rates. A composite with 1% Super C65 was also made and tested to compare the two additives at similar weight loadings. The discharge capacity comparison is shown in Figure 17 where the composite with 1% Super C65 has a significant reduction in capacity at higher rates with almost no capacity at 5C and 10C rates. A cathode composite with 1% Super C65 is demonstrated to not be feasible at rates above C/10. Therefore, the enhanced conductive percolation formed by the SWCNTs over conventional additives results in a higher capacity retention (and energy density) at higher charge-discharge rates, with significantly less additive mass, leading to a significant increase in power density.

Figure 17. Comparison of discharge capacities at C/10, 2C, 5C, and 10C for composites with 4% Super C65, 1% SWCNT, and 1% Super C65 conductive additives (results are best case scenario) (Reproduction for dissertation allowed by Elsevier [66]).
The thermal stability and safety of lithium ion battery materials can be assessed through differential scanning calorimetry (DSC), which can be used to measure the exothermic energy released from an electrode, the temperature at which it occurs, and the intensity of the reaction. All these factors relate to the contribution the materials could have towards thermal runaway[20]. Thermal runaway in lithium ion batteries typically begins in a fully charged cell at the anode where the breakdown of the solid-electrolyte-interface (SEI), around 150°C, releases heat and increases the cell temperature. The delithiated cathode then becomes unstable and releases oxygen, which, when combined with the electrolyte, fuels the reaction. Finally, the active anode material and polymer binder will then finally react at higher temperatures (around 250-300°C).

The exothermic energy released from cathode materials upon delithiation and heating using DSC can provide an indication of the material’s stability and safety, but has yet to be studied for electrode composites containing SWCNT conductive additives. Triplicate samples of each electrode design containing 1% SWCNTs or 4% Super C65 were analyzed after a complete first cycle (charge and discharge), subsequent charge to 4.3V, and float charge at 4.3V to delithiate the LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode material. Representative DSC scans for each of the LiNi$_{0.8}$Co$_{0.2}$O$_2$ composite electrodes are shown in Figure 18. The DSC peak temperature for the major exothermic reaction is similar for both conductive additives at ~225°C. However, the peak intensity, line shape, and width of the DSC peak for the 1% SWCNT sample is significantly reduced compared to the 4% Super C65 electrode, which is indicative of a lower energy release.
Figure 18. Representative DSC scans at 10°C/min for LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode composites containing 4% Super C65 (dashed line) and 1% SWCNTs (solid line) after charging to 4.3V and float charging for 12 hours. The intensities were normalized to the active cathode material mass (Reproduction for dissertation allowed by Elsevier [66]).

The exothermic energy was calculated for each cathode trial by integrating the peak region from 175 - 275 °C to encompass the major peaks and obtain a statistical comparison for the two additives. The exothermic energy released was calculated to be 1052 ± 50 J/g for the cathode using 4% Super C65, which is similar to other studies using LiNi$_{0.8}$Co$_{0.2}$O$_2$ [68]. The exothermic energy released using 1% SWCNT conductive additive was calculated to be 617 ± 31 J/g, which represents a 40% average reduction in the energy released. A summary of the DSC results are included in Table 5.
Safety of LiNi$_{0.8}$Co$_{0.2}$O$_2$ composites after overcharge is shown to be improved with SWCNT additives, which is expected with other LiMO$_2$ cathode materials as well. The reduction in exothermic energy with the use of SWCNTs is attributed to the high thermal conductivity of the SWCNTs which allows the percolation network to more readily dissipate and transfer heat within the composite, than the conventional carbons, which slows the reaction and reduces the intensity. This effect can be observed by the elimination of the secondary reaction peak by using the 1% SWCNT additive. It is important to note that higher surface area battery materials are typically considered to be detrimental in terms of the thermal stability [69, 70], however, the proper use of high purity SWCNTs (with very high surface area > 1200 m$^2$/g [71]) does not seem to be a limiting factor.

The use of SWCNTs as a conductive additive is shown to form an improved percolation network in a lithium metal oxide cathode composite over the Super C65 conductive additive. The LiNi$_{0.8}$Co$_{0.2}$O$_2$ electrode containing 1% w/w SWCNTs as a full replacement of the 4% w/w Super C65 carbon additive, had higher electrode energy density (higher active cathode mass loading), an increased coulombic efficiency, and triple the reversible capacity at a 10C discharge.
rate. DSC measurements on the two cathode compositions after being overcharged to 4.3V, showed a 40% reduction in exothermic energy released from the cathode with SWCNT conductive additives compared to the one with Super C65. Overall, the use of SWCNTs as a conductive additive promotes a percolation network at low weight loading sufficient for both improved electrochemical performance and overcharge stability.
Chapter 3. SWCNT Anode Additives

i. Introduction

As a conductive additive, SWCNTs have previously been shown to increase composite conductivity, capacity and voltage retention at high discharge rates, and thermal stability of lithium metal oxide cathode composites [66]. However, there has yet to be an analysis on the electrochemical performance and safety of traditional anode composites with SWCNT additives. Initial conductivity measurement using 0.1 % and 1% SWCNTs as a direct replacement for 5% traditional conductive carbon additive (Super P) in a MCMB anode coating, shows the largest conductivity for the composite containing 1% SWCNTs as seen in Figure 19. The conductivity measurements were performed using a 4-point probe and van der Pauw configuration. The additive weight percents are by mass of the solid components or total electrode coating mass. An image of the coatings is shown in Figure 19 with the SWCNT coating having a much lighter color because of the lower carbon weight loading. From this analysis, it is estimated at only 0.2% SWCNT additive can replace 5% Super P.
ii. Methods

Anode slurries were prepared by combining the electrode materials with N-Methyl-2-pyrrolidone (NMP) and mixing in a THINKY ARE-310 planetary centrifugal mixer at 2000 rpm. The slurries were coated onto a copper foil (18 μm, Fukuda) using a RK Control Coater 101 with an adjustable spreading blade applicator, and dried subsequently at 80°C for 1 hour. The anode slurries were mixed at a mass ratio of 91.5 wt % (MCMB and SFG-6), 8 wt % polyvinylidene fluoride (PVDF), and 0.5 wt % conductive additive (SuperP or SWCNTs) in NMP. The SWCNT material used in the current study was produced through laser vaporization and purified.
to the equivalent of the “100%” reference standard as in previous work [8,9]. The slurry containing SWCNTs was formed by first dissolving the PVDF binder in solution and then using bath ultrasonication (38.5-40.5 kHz at 40°C). The loading and thickness were matched by coating the SWCNT additive slurry at an adjustable blade height. Each composite electrode was vacuum dried at 100°C and compressed using a chrome coated roller (MTI) and the total composite mass loading was 8.5 mg/cm².

The electrodes were galvanostatically cycled using an Arbin BT-2000 at 25°C in a 2032 coin cell opposite a lithium metal foil with a Celgard 2325 separator. The electrolyte was 1.2M LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a ratio of 3:7 by volume, respectively. The analysis of capacity as a function of rate was performed between 3 – 0.005V.

Scanning electron microscopy was performed using a field emission Hitachi S-900 microscope at 2kV. Electrical conductivity (S/m) was measured on Van der Pauw geometry electrodes for the slurries after coating onto a non-conductive kapton substrate. Measurements were performed via a 4-point probe (National Instruments).

Differential Scanning Calorimetry (DSC) measurements were performed using a TA Q100 DSC, and heating at a rate of 10°C/min under a nitrogen purge. Samples were prepared by inserting Li⁺ to a capacity of 300 mAh/g after a complete charge-discharge cycle in order to have the same degree of lithiation between samples. The electrodes were removed from the coin cells in an argon-filled glove box, and sealed in an aluminum DSC pan. The specific exothermic energy
released (J/kg) was calculated by integrating under the peaks upon the heat flow data normalized
to the active anode material mass.

iii. Results and Discussion

In this study, the electrochemical performance and safety of anode composites with 0.5% w/w SWCNTs replacing 0.5% w/w Super P additives will be presented. The electrochemical performance is studied as a function of C-rate to demonstrate the effect of the SWCNTs incorporated into lithium ion battery anodes. The safety of the electrodes is determined using DSC to elucidate the implications of thermal conductivity and surface area on thermal stability.

Low weight loadings (0.5%) of traditional carbon black additives (SuperP) were replaced with SWCNTs. Because typical anodes are comprised of a graphitic carbon, a large amount of additives are generally not needed to provide percolation in the network. However, conductive additives can still provide improved performance at faster charge-discharge rates. The SEM images in Figure 20 demonstrate the difference between the two additives. The large aspect ratio SWCNTs are able to bridge gaps between active particles (Figure 20b) whereas there are large gaps visible in the composite containing SuperP (Figure 20b). The improved composite connectivity is represented in the measured conductivity values where the 0.5% SWCNT additive composite has a conductivity of 650 S/m whereas the 0.5% SuperP additive composite has a conductivity of 226 S/m.
Figure 20. Scanning electron microscopy (SEM) image of anode composites with (a) 0.5% SuperP and (b) 0.5% SWCNTs (Reproduced with permissions from Cambridge Journals [72]).

The increased composite conductivity results in improved electrochemical performance as well. Figure 21a shows the electrochemical comparison of the two composites at increasing discharge rates which demonstrates an approximately 20% higher capacity retention at higher C-rates (above C/2) resulting from the use of the highly conductive SWCNT additives.
Figure 21. Electrochemical testing (a) at increasing discharge rates and DSC (b) of 0.5% superP additive composite (squares) and 0.5% SWCNT additive composite (triangles) (results are best case scenario) (Reproduced with permissions from Cambridge Journals [72]).

The thermal stability of the composites was measured using DSC to measure the effect of the SWCNT additive. Figure 21b shows that the replacement of traditional conductive additives with SWCNTs results in a significant lowering of the major peak intensity as well as a reduction in peak width. This gives rise to an approximately 35% lower exothermic energy release for the
0.5% SWCNT additive composite (709 J/g) than the 0.5% superP additive composite (1105 J/g). The improvement in electrochemical performance and thermal stability of the composites is similar to those found in previous studies using SWCNTs in cathode composites[66]. The increased rate capability in the electrochemical cell is attributed to the increase in composite electrical conductivity. The lowered exothermic reaction measured in the DSC is attributed to the increased thermal conductivity of the SWCNTs allowing for heat dissipation within the composite. The low amount of SWCNT additive does not significantly add to the SEI formation on the anode, and thus the thermal conductivity can improve the thermal stability. Therefore, the use of SWCNTs as a conductive additive in MCMB anode composites demonstrated improvements in rate capability and thermal stability of the electrode at low weight loadings.
Chapter 4. Energy Density Improvements – SWCNT Additive composites

i. Introduction

There exists a number of ways to improve the energy density of a lithium ion battery. Energy density is typically stated in terms of Wh/kg which is the energy provided by the active materials (the materials shuttling lithium ions) divided by the entire mass of the battery which includes packaging, electrolyte, current collectors, binders, and conductive additives. Increases in energy density can be made by decreasing component masses and/or increasing the energy of the battery by changing active material loading or structure.

The majority of research to improve energy density has focused on increasing the active materials capacity and/or voltage. A summary of battery active material capacity and voltage vs. lithium is shown in Figure 22. However, the state-of-the-art cathode capacity is still only between 180-250 mAh/g which is lower than the standard anode which has a capacity around 300-330 mAh/g[73]. Therefore, in order to capacity match the electrode, a higher cathode loading is needed which lowers the battery energy density. Higher voltage cathodes show promise, but run into electrolyte degradation problems above 4.6V[74].
Figure 22. Specific capacity and voltage of lithium ion active cathode and anode materials (Reproduction for dissertation allowed by The Royal Society of Chemistry (RSC)[25]).

The use of higher capacity anode materials, such as Si and Ge, has been shown to improve the energy density of the battery with specific capacities reaching 3000 mAh/g for Si[75, 76]. The full battery energy density increase is typically only around 10% due to the heavy copper current collector and the low capacity cathodes[77]. The benefit of the high capacity anode is not realized above 1000 mAh/g because the cathode capacity is not high enough to match the higher anode capacity in standard designs. The typical Si based anodes are restricted to being thinly coated on much heavier copper current collectors which leads to the marginal gains in energy density.
Thicker cathode composites would enable capacity matching to higher capacity anode materials as well as improve electrode energy density by reducing the relative mass of the aluminum current collector shown in Figure 23(a). Initial modeling of a lithium ion battery where just the thickness of the cathode is increased versus a standard anode was performed using constrained optimization model with WhatsBest! Microsoft Excel macro. The model optimized the energy density of the cell by changing the number of layers that would fit in a 64350 battery at a particular matched anode and cathode thickness. The cathode thickness constraint was increased to obtain the energy density improvement by thickening the cathode as shown in Figure 23(b).
Figure 23. (a) Electrode engineering by composite thickening diagram. (b) Energy density versus cathode thickness for standard NCA cathode and MCMB anode composites (Original figure and modeling by the author).
The model results show a significant increase in energy density with thickness until around 150 um where the mass of the current collectors starts to become less significant. Increasing the thickness from a typical maximum around 100 um to 200 um would boost the energy density of the cell by 25%.

At higher composite loadings, the electronic and ionic conductivity of the composite plays a larger role as electrons much travel through a thicker composite to the current collector and electrolyte must be present throughout the composite to enable lithium ion conduction. This work investigates thicker cathode composites with standard carbon black and SWCNT additives to determine the capability to increase loading and the effect conduction has on the electrochemical performance.

ii. Methods

Cathode slurries were prepared by combining the electrode materials with N-Methyl-2-pyrrolidone (NMP) and mixing in a THINKY ARE-310 planetary centrifugal mixer at 2000 rpm. The slurries were coated onto an aluminum foil (18 μm, Fukuda) using a RK Control Coater 101 with adjustable spreading blade applicator, and dried subsequently at 80°C for 1 hour. The control cathode slurry incorporating Super C65 (TIMCAL) was mixed at a mass ratio of 92 wt % LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA), 4 wt % KYNAR Powerflex polyvinylidene fluoride (PVDF), and 4 wt % Super C65 in NMP. Cathode slurries integrating SWCNTs as a conductive additive replacement were mixed with 4% PVDF binder for all sample and the amount of active material was adjusted for the percentage SWCNTs used (95NCA:1SWCNT, 94.5NCA:1.5SWCNT, 94NCA:2SWCNT). The SWCNT material used in the current study was produced through laser
vaporization and purified to the equivalent of the “100%” reference standard as in previous work [41, 42]. The slurry containing SWCNTs was formed by alternating bath ultrasonication (38.5-40.5 Hz at 40°C) and planetary centrifugal mixing of the SWCNTs in NMP and PVDF solution to improve the dispersion and final mixing with LiNiCoAlO₂. The ratio of concentration of SWCNTs in NMP (mg/mL) was kept constant to ensure proper SWCNT dispersion, and the height of the adjustable blade coater was adjusted to obtain the desired areal loading. Each composite electrode was then vacuum dried at 100°C and compressed using a chrome coated roller (MTI) to reduce the thickness by 30-40%. Thickness measurements were made on cathode cross-sections using a Nikon optical microscope with a Nomarski prism at 200x magnification.

The electrodes were galvanostatically cycled using an Arbin BT-2000 at 25°C in a LiNiCoAlO₂ vs. Li/Li⁺ cell using a lithium metal foil in a 2032 coin cell configuration with a Celgard 2325 separator. The electrolyte was 1.2M LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a ratio of 3:7 by volume, respectively. The analysis of capacity as a function of rate was performed between 3.0 - 4.3V vs. (Li/Li⁺)/V with a constant voltage step at 4.3V until the current dropped to 5% of the original current. The charge rate was at C/10 for the first cycles, and was a C/5 rate for subsequent cycles. The discharge rate was then adjusted at varying rates (C/10, C/5, C/2, 1C). Scanning electron microscopy was performed using a field emission Hitachi S-900 microscope at 2kV.
iii. Results and Discussion

Typical areal loading capacities for commercial lithium ion battery electrodes are around 2 mAh/cm\(^2\) with a thickness in the range of 60 µm, and go as high as 4 mAh/cm\(^2\) and 100 µm thick. Batteries containing higher areal loadings are considered for energy density only and are used for applications that allow for slow charge-discharge rates. At faster discharge rates, a higher voltage drop and lower capacity is found due to resistive losses caused by a thicker low conductivity composite. SWCNTs have been shown to improve rate capability and conductivity of composites previously at a low loading of 1%. However, a higher percentage of SWCNTs may be necessary to improve the rate performance of thicker and higher areal loading electrodes. A LiNiCoAlO\(_2\) (NCA) cathode composite at a loading of 4 mAh/cm\(^2\) or 100 µm in thickness with 4% carbon black additive vs. 1.0, 1.5, and 2% SWCNT additive is shown in Figure 24. Previous work compared 1% SWCNTs with 4% carbon black at a low loading of ~1.6 mAh/cm\(^2\), and demonstrated similar capacities up to a 2C rate with the SWCNT composite having higher capacity and voltage retention at 5C and 10C rates. However, at a higher areal loading of 4 mAh/cm\(^2\) a higher capacity was found starting at a 1C rate. This demonstrates the importance of composite conductivity at higher areal loadings. When the weight loading of SWCNT additive is increased further, a higher capacity was measured at all rates and a slight improvement is seen going from 1.5% to 2.0% SWCNTs at a 1C rate.
Figure 24. Discharge capacity of LiNiCoAlO$_2$ (NCA) with 4.0% Super C65 (carbon black) and 1.0, 1.5, and 2.0% SWCNTs (results are best case scenario).

According to the modeling of electrode thickness versus electrode energy density shown in Figure 14, the significant increase in energy density ends at around 200 µm or around a 8 mAh/cm$^2$ loading before asymptotically approaching a maximum. Therefore, composites with 1% SWCNTs and 4% carbon black were coated at 8 mAh/cm$^2$ to assess the higher energy design and test the cycleability at low rates. However, as seen in Figure 25, the composite with carbon black additives suffered from poor adhesion and composite flexibility. Therefore, a composite with that high of a loading on standard aluminum foil is not practical and it wasn’t possible to test the electrode. The composite containing SWCNTs was flexible and well-adhered to the current collect owing to the ability of the SWCNTs to entangle particles, uptake the polymer binder, and create long range connectivity as shown in the SEM image. These images...
demonstrate the improved flexibility of electrodes using SWCNT additives which could also lead to improved cycling performance. The current work did not extensively investigate cycling, but composites with SWCNT additives did not show degradation in performance compared to traditional additives at modest cycling numbers. Further long term studies are warranted to investigate the effect of SWCNTs on cycling.
Figure 25. Images of 8 mAh/cm² composites with (a) 4% carbon black additive and (b) 1% SWCNT additive. (c) Cross-section of 8 mAh/cm² composite and (d) SEM of NCA composite with 1% SWCNTs (Original photographs by the author).
The 8 mAh/cm$^2$ NCA cathode with 1% SWCNT additives was cycled versus both lithium and a capacity matched anode at a slow rate (C/10) to determine the cyclability of higher areal loading composites (Figure 26). The high loading composite had little to no fade when over 30 cycles for both cells and demonstrates the potential for using thicker composites with SWCNT additives in high energy designs.

**Figure 26.** Cycling of NCA cathode with 1% SWCNT additive at a 8 mAh/cm$^2$ loading versus lithium metal (black) and a capacity matched MCMB composite (red) (results are best case scenario).
Electrodes at 4 and 8 mAh/cm² areal loadings with 2% SWCNT were compared to monitor discharge rate limit for maintaining capacity using thicker composites (Figure 27). The cycling results at increasing discharge rates demonstrate a significant drop in capacity at rates above 1C. However, similar discharge capacities were achieved up to a c/2 rate which is a common discharge rate for higher energy applications.

![Figure 27](image.png)

**Figure 27.** Comparison of 4 and 8 mAh/cm² NCA cathodes with 2% SWCNT additives at increasing discharge rates (results are best case scenario).
These results demonstrate that increased weight loadings of SWCNT additives can significantly improve rate performance of higher areal capacity NCA composites compared to traditional composites with carbon black additives. At extremely high loadings (8mAh/cm²), SWCNT additives are necessary to provide composite mechanical stability and adhesion to the Al current collector. These high loading composites cycled well at slow rates using 1% w/w SWCNT additives, and increasing additive percentage to 2% w/w demonstrated equivalent discharge rate performance up to a 2C rate. At the higher loadings, the rate performance may be further enhanced by optimizing ionic conductivity through controlled electrode porosity. Overall, the SWCNT additives can allow for significantly higher composite areal loadings which can result in up to a 20-25% increase in battery energy density.
Chapter 5. Energy Density Improvements – Composites on CNT Support

i. Introduction

Other methods to increase the energy density of battery composites using SWCNTs are to use a free-standing SWCNT paper as a current collector replacement, where the composite slurries would be coated onto SWCNT papers, or form a free-standing composite, where the active materials and SWCNTs are mixed and coated or filtered to form a three-dimensional composite. In either case, the increase in energy is due to the complete elimination of the current collector which is particularly beneficial on the anode side by replacing the dense copper foil. Previous studies have looked at using SWCNTs as current collectors with next generation materials, such as Si, Ge, and vanadium, but there has yet to be studies looking at the energy density gains using SWCNTs as current collectors with today’s SOA materials[78, 79].

In order to quantify an impact on energy density, the specific capacities of the active materials, NCA and MCMB, were compared to the total electrode specific capacities including the current collector, binder, and conductive additive at different areal loadings. The efficacy of CNTs current collectors is only recently being pursued[80]. The total electrode specific capacity gives a much more accurate indication of the actual effect on energy density of a full battery because all of the components of the electrode are included. Figure 28a compares the specific capacity of NCA material to electrode specific capacity when coated on Al foil or CNT papers.
The specific capacity of the NCA material is the same for either current collector since this is the active material capacity around 185 mAh/g regardless of the current collector used. As the areal electrode loading is increased from 2 to 8 mAh/cm$^2$ the relative mass of the current collector is decreased thus increasing electrode energy density. However, the CNT paper is a lower percentage of the total electrode mass to begin with therefore the change in electrode capacity
with loading isn’t as significant. By using the CNT paper as the current collector, a 28% improvement in electrode capacity is found at the standard loading of 2 mAh/cm² and has only a slight improvement at higher 8 mAh/cm² loadings of 8%. Equivalent electrode energy densities can be reached with a 2 mAh/cm² coating on SWCNTs versus an 8 mAh/cm² coating on Al allowing for a thinner coating which improves power capability simultaneously.

The comparison of MCMB specific capacity to MCMB electrode capacity coated on Cu or CNTs is shown in Figure 28b and demonstrates the impact of replacing the heavy copper current collector. There is a significant drop in specific capacity when including the copper current collector at standard 2 mAh/cm² loadings from 330 mAh/g for MCMB to 86 mAh/g for MCMB coated on Cu compared to 247 mAh/g for MCMB on CNTs. Therefore, replacing the Cu current collector with CNTs can nearly quadruple the electrode capacity at 2 mAh/cm², double the electrode capacity at 4 mAh/cm², and still have a 50% improvement at 8 mAh/cm². Thus, there is a considerable energy density gain that can be garnered by using CNT current collectors as a replacement for conventional copper foil. In addition there is potential benefit from CNTs having a zero volt state of charge and increased depth of discharge below 2.5V compared to traditional copper current collector.

The effect of CNT paper properties such as, purity, conductivity, and CNT type on current collector performance is not well understood. The purity of CNT materials can typically be related back to the performance of the material in a variety of devices, and is dependent on synthesis method and post-processing. The presence of metallic impurities may cause undesirable side reactions or be corroded when used as a current collector[81]. The conductivity
of CNT papers can vary significantly with CNT type (e.g. single, multi, double wall CNTs), alignment, and processing (doping, densification)[82, 83]. Currently, high conductivity bulk CNT papers are an order of magnitude lower in conductivity to copper, but have reached conductivity values equal to that of titanium which is a common lithium ion battery current collector[84]. This study investigates using commercially available CNTs as current collectors for traditional lithium ion battery electrode composites. A purification technique was developed to determine the effect of purity on current collector performance.

ii. Methods

Electrode slurries were prepared by combining the electrode materials with N-Methyl-2-pyrrolidone (NMP) and mixing in a THINKY ARE-310 planetary centrifugal mixer at 2000 rpm. The slurries were coated onto commercial CNTs (Nanocomp AA-0043) using a RK Control Coater 101 with adjustable spreading blade applicator, and dried subsequently at 80°C for 1 hour. Coatings on as-received and purified Nanocomp CNTs were compared. The CNT sheet was burned in air to 560 °C at a 10 °C min⁻¹ ramp rate, and resulted in a >50% w/w reduction in the mass of the CNT sheet material. A concentrated HCl (37.5% w/w HCl in H₂O – Sigma Aldrich) rinse was used to remove the particles on the surface where the CNT sheet was allowed to soak for an additional 15 minutes with slight agitation before being rinsed with DI H₂O for 30 minutes. The CNT sheet was then dried in a vacuum over at 100 °C overnight. The slurries were mixed at a mass ratio of 92 wt % LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂, 4 wt % KYNAR Powerflex polyvinylidene fluoride (PVDF), and 4 wt % Super P (Timcal) for the cathode and 91.5wt % MCMB-SFG-6, 8 wt % PVDF and 0.5 wt % Super C65 in NMP. Each composite electrode was then vacuum dried at 100°C and compressed using a chrome coated roller (MTI).
The electrodes were galvanostatically cycled using an Arbin BT-2000 at 25°C vs. Li/Li⁺ cell using a lithium metal foil in a 2032 coin cell configuration. The electrolyte was 1.2M LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a ratio of 3:7 by volume, respectively. The analysis of capacity as a function of rate was performed between 2.5 - 4.3V for cathode electrodes and 0.005 – 3V for anode electrodes.

### iii. Results and Discussion

Purification methods were investigated for commercial Nanocomp CNTs. As seen in Figure 29(a), the as-received CNTs contain a significant amount of carbonaceous and metallic impurities. Initial attempts of purification followed techniques described previously that are used to purify SWCNTs where the CNT paper is refluxed in a nitric acid and HCL bath to remove metallic impurities. The paper is then thermally oxidized to remove non-CNT carbonaceous impurities. This process did not significantly improve the CNT paper purity. As can be seen in the photograph inset in Figure 29(a), even when the paper is exposed to concentration HCL no reaction or metallic dissolution occurs. This is most likely due to carbon coating the metallic particles and preventing dissolution. Therefore, the CNT paper was first thermal oxidized as seen in Figure 29(b). The high temperature burn appears to have removed the carbonaceous impurities but the metal is still present. When the burned paper is placed in concentrated HCL, a solution color change is instantly visible due to metallic dissolution. After neutralizing the paper with water rinses, the purified paper is absent of both metallic and carbonaceous impurities as observed in Figure 29(c).
Initially, CNT current collectors were used to replace copper current collectors on the anode. A standard composite using MCMB active material, PVDF binder, and carbon black were coated onto a commercial CNT paper from Nanocomp Technologies. The coating method was the same as would it would be with a copper current collector, and the composite appeared well adhered to the CNT paper. Cross sectional SEM images of a cleaved MCMB composite coated on purified CNTs can be seen in Figure 30 with increasing magnification. The images show a uniform CNT paper that is compliant with the composite and can compress to provide enhanced contacting. Even in areas that became delaminated due to electrode cleaving, the SWCNTs can be seen bridging the gap between the CNT paper and the composite in the higher magnification image. Therefore, a CNT paper may be able to provide electrical contact even after partial composite delamination.
Figure 30. Cross-sectional images of MCMB composite coated on CNT paper with increasing magnification (Images captured by Christopher Schauerman).

The first cycle voltage profiles of MCMB anode composites on as-received and purified CNT and copper current collectors are shown in Figure 31a. The extraction capacities of the MCMB composites coated on Cu and purified CNTs are equivalent up to typical cut-off voltages of 1.0 V of ~ 300 mAh/g. The composite on purified CNTs has a slightly higher capacity above 1.0 V due to a small amount of lithium ion storage in the CNT paper. However, the extraction capacity of the composite coated on the as-received (unpurified) CNT paper had a lower capacity of ~ 260 mAh/g. This result demonstrates that the CNT paper must be of high purity, absent of metallic and carbonaceous impurities, to be utilized as a current collector in lithium ion batteries.
Figure 31. (a) First cycle voltage profiles for MCMB anode composites coated on Cu, as-received CNTs, and purified CNTs (results are best case scenario).
The first cycle coulombic efficiency of the anode composites on CNTs was measured to be much lower (~65%) compared to MCMB coatings on Cu. The additional SEI formation can be seen in the insertion voltage curves where a plateau is present around 0.75 V for the composite on CNT current collectors. The higher first cycle loss is common for free-standing anodes where the CNTs act as the active material and current collector, and is due to the high surface area CNTs. However, the loss in a free-standing CNT anode is significantly greater with coulombic efficiencies around 20%. A reduction in SEI formation when using CNTs as an anode current collector can be achieved through pre-lithiation or surface area reduction which has recently been studied.

Evaluation of purified CNT sheets to support a standard cathode composite consisting of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 (NCA), PVDF binder, and carbon black has been performed. Although the mass savings is less significant, the CNTs are still less dense than Al current collectors and improve energy density as previously discussed. The use of CNTs as a cathode current collector should not have the issue of excess SEI formation and first cycle loss as the CNTs are anodic in nature and SEI formation on the cathode isn’t as significant. The electrochemical results shown in Figure 32 demonstrate the ability to use CNT current collectors on the cathode as well. The specific active capacity was measured to be around 185 mAh/g which is standard for NCA composites. The coulombic efficiency is demonstrated to be around 90% which is comparable to composites coated on Al foil. The rate capability of NCA composites on Al and CNT current collectors was measured at increasing discharge rates. The cycling and capacities were similar with the composite on CNTs having a slightly higher capacity demonstrating that CNT current collectors can provide equivalent rate performance to Al.
Figure 32. (a) First cycle voltage profiles for LiNiCoAlO$_2$ cathode composite coated on CNTs. (b) Cycling performance at varying discharge rates comparing NCA composites coated on Al vs. CNTs (results are best case scenario) (Inset image taken by Jason Staub).
These results demonstrate the ability to coat standard cathode and anode slurries onto CNT papers to enhance energy density. Composites coated on CNTs had similar performance compared to coatings on metal current collectors. The resulting mass decrease from using CNT supports results in a 5-10% increase in energy density for a battery containing cathode composites on CNTs and a 20-30% increase for battery containing anode composites coated on CNTs based on previous full cell calculations[85].
Chapter 6. Energy Density Improvements – SWCNT Si-Ge Free-standing Supports

i. Introduction

The use of nanomaterials in lithium ion batteries has led to significant gains in the electrochemical performance of battery materials by enabling faster ionic conduction and stability of active materials with cycling. While much of the focus is on decreasing the size of active cathode and anode particles to the nanoscale, improved rate capability, cycling, and energy density has been realized through the use of highly conductive and lightweight nanomaterials as conductive additives or free-standing electrode supports.

SWCNT free-standing anodes (absent of binder or current collector) have been demonstrated to have high specific capacities (500-1000 mAh/g), but suffer from an extreme 1st cycle loss and sloping voltage profile[4]. Therefore, SWCNTs have recently been used as a free-standing support for active cathode and anode particles where the high conductivity, flexibility, and lightweight nature of SWCNT papers can be utilized[5]. Cathode composites mixing SWCNTs and lithium metal oxide materials, and anode composites coating or mixing high capacity Ge and Si materials have demonstrated increases in energy density (due to the removal of binder and heavy Cu current collector) as well as improved rate capability and cycleability due to the SWCNT morphology[6]. Yet, the safety of these new generation free-standing electrodes has yet to be investigated.
In this work, silicon was deposited onto SWCNTs and high energy and power Ge-NP:SWCNT electrodes to improve electrochemical performance by tailoring the nanostructured anodes, in addition to improving the safety of free-standing anodes by developing a passivation layer for high surface area SWCNTs. The impact of additional high capacity material within the Si-Ge-NP:SWCNT electrodes was evaluated by materials characterization through microscopy and spectroscopy techniques and electrochemical testing to study voltage effects and rate capability. Additionally, the safety of silicon-passivated SWCNT anodes was determined by DSC to elucidate the implications of thermal conductivity and surface area on thermal stability of these nanomaterials anodes.

ii. Methods

Carbon encapsulated-germanium nanoparticles were synthesized by a modified chemical vapor deposition (CVD) process that has been previously reported.[86] In short, a phenyltrimethylgermane precursor was injected at 1 mL hr\(^{-1}\) into a CVD reactor at 800°C in an argon environment at ambient pressure to synthesize the nanoparticles. The hybrid anodes were prepared by combining relative weight fractions of purified SWCNTs and Ge-NPs measured by a Mettler Toledo high precision balance with 0.1 \(\mu\)g accuracy, sonication in N-cyclohexylpyrrolidinone for 45 minutes, and filtration on a PTFE filter to form the free-standing electrodes.

Free-standing hybrid electrodes were prepared by depositing silicon on SWCNT and germanium nanoparticle SWCNT electrodes with a low-pressure CVD (LPCVD) process. The adapted
technique was at 500 ºC at 1 Torr with 50 sccm of silane, with deposition times of 15 and 30 minutes to vary weight loading[10].

The electrodes were galvanostatically cycled using an Arbin BT-2000 at 25°C in a 2032 coin cell opposite a lithium metal foil with a Celgard 2325 separator. The electrolyte was 1.2M LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) at a ratio of 3:7 by volume, respectively. The analysis of capacity as a function of rate was performed between 3 – 0.005V.

Scanning electron microscopy was performed using a field emission Hitachi S-900 microscope at 2kV. Electrical conductivity (S/m) was measured on Van der Pauw geometry electrodes for the slurries after coating onto a non-conductive kapton substrate. Measurements were performed via a 4-point probe (National Instruments).

Differential Scanning Calorimetry (DSC) measurements were performed using a TA Q100 DSC, and heating at a rate of 10°C/min under a nitrogen purge. Samples were prepared by inserting Li⁺ to a capacity of 300 mAh/g after a complete charge-discharge cycle in order to have the same degree of lithiation between samples for the silicon coated SWCT samples. The electrodes were removed from the coin cells in an argon-filled glove box, and sealed in an aluminum DSC pan. The specific exothermic energy released (J/kg) was calculated by integrating under the peaks upon the heat flow data normalized to the active anode material mass. For the Si, Ge, and SWCNT hybrid samples the lithium insertion was performed to the same voltage of 0.005V to fully lithiate the anodes and the DSC results were reported per capacity (J/mAh).
iii.  Results and Discussion

Silicon was coated on free-standing SWCNT papers at deposition times of 15 and 30 minutes to provide increasing loadings of Si. Figure 33 shows the SEM images of SWCNT papers with no silicon (0 min) and Si deposited at 15 and 30 minutes. The images show SWCNT bundles being covered with Si and pores in the paper being filled with Si as well.

![SEM images of SWCNT papers](image)

**Figure 33.** SEM images of a free-standing SWCNT paper (0 min) and SWCNT papers coated with Si for 15 minutes and 30 minutes (Reproduced with permissions from Cambridge Journals [72]).

The electrochemical data for the three electrodes are shown in Figure 34a. As the amount of Si is increased, the SEI formation on the 1st Li⁺ insertion cycle decreases as can be seen by the reduction in the plateau around 0.9V. The extraction capacity also increases with higher Si loadings with capacity around 2300 mAh/g for the highest Si loading. The coulombic efficiency increases from 18% for the pure SWCNT paper, to 55% for the 15 min sample, to greater than 90% for the 30 minute sample. The SEI formation and coulombic efficiency improvements are a
function of the reduction in surface area by coating the SWCNTs and pores with Si. The surface area of the pure SWCNT paper is 956 m$^2$/g and is reduced to 113 m$^2$/g for the 30 minute sample.

The reduction in SEI formation was found to improve the safety of these electrodes as measured by DSC and seen in Figure 34b. The pure SWCNT paper has a significant SEI formation due to its high surface area which results in a lower reaction initiation temperature and a greater reaction intensity. Therefore, a pure SWCNT paper could initiate a thermal runaway reaction at a lower temperature.
Figure 34. (a) 1st cycle voltage profiles and (b) DSC of lithiated of a free-standing SWCNT paper (0 min) and SWCNT papers coated with Si for 15 minutes and 30 minutes (results are best case scenario) (Reproduced with permissions from Cambridge Journals [72].
As the Si loading is increased to 15 minutes, the main peak temperature is shifted to higher temperatures, but the exothermic energy released for the 15 min sample (3871 J/g) is comparable to the pure SWCNT paper (2910 J/g). However, as the loading is increased to 30 min, the lower SEI formation results in a shift in the starting reaction temperature and a significant reduction in peak intensity and exothermic energy released (1581 J/g). This approach shows progress in stabilizing high energy Si-SWCNT anodes, consistent with MCMB composite safety.

Prior electrochemical performance on Ge-NP:SWCNT electrodes demonstrated stable cycling at modest cycling rates.[86] The rate capability of the hetero-hybrid containing both silicon and germanium was compared with a Ge-NP:SWCNT electrode versus lithium at currents of 50 to 1000 mA g\(^{-1}\). Figure 35 shows the first two conditioning cycle capacities at a 3 V vs. Li/Li\(^+\) cut-off voltage with the remaining cycles having a cut-off voltage of 1.5 V vs. Li/Li\(^+\) to focus on the lithium storage in Si and Ge active materials. The hetero-hybrid electrode has a capacity over 1200 mAh g\(^{-1}\) at low cycling rates as compared to the Ge-NP:SWCNT:Ti hybrid with a capacity just over 800 mAh g\(^{-1}\). Additionally the hetero-hybrids have an increase in extraction capacity from cycle 1 to 2 as seen with other electrodes containing germanium.[86] As the extraction current is increased to 1000 mA g\(^{-1}\), the hetero-hybrid electrode extraction capacity is reduced to 500 mAh g\(^{-1}\). The larger change in capacity of the hetero-hybrid, as compared to the Ge-NP:SWCNT electrode, as extraction current is increased beyond 200 mA g\(^{-1}\) is suggestive of the diminished storage contribution of the silicon at the higher extraction rates.
Figure 35. Extraction capacities of Ge-NP:SWCNT hybrids and Si-Ge-NP:SWCNT hybrids as extraction current is increased from 50 mA g\(^{-1}\) to 1000 mA g\(^{-1}\). The first two conditioning cycles had a cut-off voltage of 3 V vs. Li/Li\(^+\) and the following cycles had a cut-off voltage of 1.5 V vs. Li/Li\(^+\) (results are best case scenario) (Reproduction for dissertation allowed by Elsevier Journals[87]).

This also highlights the need to balance the constituent materials in order to optimize the electrochemical performance based upon storage capacity, rate capability, and coulombic efficiency. Overall, the hetero-hybrid has a higher first cycle coulombic efficiency and a higher capacity at slow extraction currents, when compared to the Ge-NP:SWCNT hybrid electrode. Also, the hetero-hybrid retains a similar extraction capacity, up to 500 mAh g\(^{-1}\), as that of the Ge-NP:SWCNT hybrid at faster extraction currents.
Demonstration of increased storage capacity in nanomaterial anodes is critical, but it is also important to evaluate the safety of novel anodes. The thermal stability of the various types of hybrid free-standing anodes and a SWCNT anode were measured by differential scanning calorimetry (DSC). The DSC curves in Figure 36 were normalized to electrode capacity to compare anodes of varying capacities[88].

![Differential Scanning Calorimetry (DSC) for SWCNT, Ge-NP:SWCNT, Si-Ge-NP-SWCNT anodes after one complete cycle and lithiation to a cell potential of 5 mV vs. Li/Li⁺ (results are best case scenario) (Reproduction for dissertation allowed by Elsevier Journals[87]).](image-url)
The pure SWCNT paper has significant SEI formation due to its high surface area which results in a lower reaction initiation temperature of 125°C and a greater reaction intensity of 7.06 J mAh\(^{-1}\), as compared to conventional MCMB composites with a value of 5.14 J mAh\(^{-1}\). Therefore, a pure SWCNT paper would initiate a thermal runaway reaction at a lower temperature. When SWCNTs and Ge-NPs are mixed, the exothermic energy released is reduced to 4.26 J mAh\(^{-1}\) compared to 7.06 J mAh\(^{-1}\) for the pure SWCNT sample. When Si is coated on the Ge-NP:SWCNT electrode the reduced SEI formation results in a shift in the starting reaction temperature to 160°C and a significant reduction in peak intensity and exothermic energy released (2.77 J mAh\(^{-1}\)). The exothermic release for the hetero-hybrid electrode is reduced by almost half when compared to conventional MCMB composites. Thus, the silicon deposition approach to free-standing anodes shows progress in tailoring nanomaterial anodes for higher capacities in conjunction with improved safety, as evidenced by an exothermic release reduction of almost half while the electrode capacity for the anode is more than quadruple that of conventional MCMB anodes.
Table 6 summarizes electrochemical performance and safety of the anodes shown in Figure 35, highlighting the trend of a reduction in surface area and heat flow with an increase in first cycle coulombic efficiency and capacity. The addition of silicon has benefits for both performance and safety aspects of free-standing anodes.

<table>
<thead>
<tr>
<th></th>
<th>Surface Area (m² g⁻¹)</th>
<th>Coulombic Efficiency (%)</th>
<th>Capacity (mAh g⁻¹) @ 50 mA g⁻¹</th>
<th>Heat Flow (J mAh⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs</td>
<td>956</td>
<td>20</td>
<td>550</td>
<td>7.062</td>
</tr>
<tr>
<td>Ge-NP:SWCNT:Ti (80:16:4)</td>
<td>74</td>
<td>70</td>
<td>840</td>
<td>4.261</td>
</tr>
<tr>
<td>Si-Ge-NP:SWCNT (28:57:12:3)</td>
<td>50</td>
<td>86</td>
<td>1225</td>
<td>2.768</td>
</tr>
</tbody>
</table>

Table 6. Summary of the surface area, coulombic efficiency, capacity, and heat flow for the electrode series (Reproduction for dissertation allowed by Elsevier Journals[87]).

The electrochemical performance and safety of free-standing SWCNT electrodes was shown to improve with higher Si loadings. The reduction in surface area, which reduces the SEI formation, improved coulombic efficiency, increased the temperature required for a thermal reaction, and lowered the overall exothermic energy released. The proper processing of the electrode greatly increased the energy density of the anode and puts the thermal stability on par with traditional composites.
**Summary and Acknowledgements**

This chapter demonstrated the potential to engineer lithium ion battery electrodes using SWCNTs. The use of SWCNTs as a conductive additive in both anode and cathode composites improved rate capability with a small weight percentage of SWCNTs that were properly mixed throughout the composite. DSC results demonstrated a 35-40% reduction in exothermic energy released when incorporating SWCNT additives as compared to traditional carbon black additives. The use of SWCNT additives allowed for increased cathode areal loadings which can increase electrode energy densities up to 50% by reducing the relative mass of the current collector. The SWCNT additives provided a mechanically robust composite with improved rate performance with higher SWCNT weight loadings. The use of CNT current collectors was optimized by purification of commercial CNT sheets. The rate performances of CNT current collectors were found to be equivalent to metallic based current collectors. Entire battery energy density can be improved by 5-30% by replacing the heavy metal current collectors. Advance free-standing anodes incorporating SWCNTs with high capacity silicon and germanium were measured to have high capacities. Improved rate performance was determined through the use of germanium, and silicon coated anodes had higher coulombic efficiencies and higher capacities. Coating of the electrodes with silicon decreased surface area which leads to a lower exothermic energy release as measured by DSC.

A summary of the DSC data is plotted in Figure 37 as a function of active material capacity. The measurements are plotted as a function of capacity which will ultimately determine how much active material mass is used in the battery to reach a particular capacity when matching with the cathode. The plot summarizes DSC data where the exothermic energy released (the integrated
area under the curve) is plotted versus the maximum peak intensity to compare thermal reactivity or stability of battery materials and electrodes on a single graph. This plot will be referred to as a thermal stability plot. The plot is similar to a Ragonne plot in which power is plotted versus energy, but the Ragonne plot describes the electrochemical performance of energy storage systems whereas the thermal stability plot is related to the safety of battery materials. In the Ragonne plot, the ultimate goal is to move into the upper right hand corner of the plot where both energy and power are maximized. The opposite is true for the thermal reactivity plot where the ideal point is in the lower left hand corner of the plot which minimizes thermal reactivity and maximizes safety. This plot provides a comparison of material thermal reactivity on a single plot which can be used to monitor and optimize battery material safety and provide guidance to decision makers. The plot summarizes the DSC data from this work which demonstrates the high thermal reactivity of cathodes compared to anodes and illustrates the need to improve cathode thermal stability. Arrows are provided for guidance describing mechanistic changes to electrode thermal reactivity.
Figure 37. Thermal reactivity plot as a function of mass and capacity comparing samples with SWCNT and carbon black additives, and those incorporating CNT supports (Figure created by the author).
The results demonstrate two main trends when using SWCNTs in battery electrodes. When used as an additive, a reduction in exothermic energy and power can be seen for both the anode and cathode and is attributed to increased composite thermal conductivity. The small weight percentage of SWCNTs as an additive does not increase SEI formation as similar coulombic efficiencies were measured. However, when using SWCNTs as a current collector to support high capacity nanomaterials, the surface area of the electrode has a large impact on the thermal stability. The pure SWCNT anode has the highest surface area which leads to a significant amount of SEI formation and results in a high thermal power and large exothermic energy release. As the surface area is decreased by incorporation of high capacity Ge nanoparticles and coated with Si, the thermal stability of the electrode is significantly improved.

The author would like to acknowledge Christopher Schauerman for his help in taking composite conductivity measurements, and development of the commercial CNT purification method. The author also acknowledges Roberta DiLeo for preparing and measuring the electrochemical performance of the free-standing electrodes incorporating silicon, germanium, and SWCNTs.
TOPIC III. END-OF-LIFE AND BATTERY MANAGEMENT

Overview

This chapter discusses the end-of-life (EOL) management of lithium ion battery materials. The work focuses on LiFePO$_4$ and a new concept in EOL management called *refunctionalization*. Refunctionalization is the treatment of active materials in order to regain electrochemical performance at EOL. The advantage of refunctionalization is the elimination of the re-synthesis step for active materials from virgin materials or those recycled to the elemental level. This technique is particularly useful in the case of cathode materials with low value recoverable elements (Fe, Mn) such as LiFePO$_4$. Refunctionalization of LiFePO$_4$ at EOL was studied through electrochemical and chemical lithiation. The environmental implications were studied by modeling the embodied every of refunctionalized LiFePO$_4$ versus cathode produced from virgin and recycled materials. This work is being submitted for publication.
Chapter 7. LiFePO₄ Remanufacture and Refunctionalization

i. Introduction

The use of lithium ion batteries in portable consumer electronics has become nearly ubiquitous and significant adoption is predicted in electric vehicle and renewable energy storage. [89] Worldwide sales of lithium ion batteries are estimated to nearly triple in the upcoming years and surpass lead acid sales. [90] This will lead to an increase in lithium ion batteries that are produced and eventually enter the waste stream. Therefore, end-of-life (EOL) management is a critical concern warranting future studies today.

To understand the impacts toward sustainability, the full life-cycle impacts must be taken into account. The life-cycle of lithium ion batteries follows that of most products: synthesis and use of materials to produce the cells and packs, use phase in a device, and ultimate end-of-life (EOL). [91] Most life-cycle studies on batteries used in electric vehicles have focused on quantifying use phase impacts and improving device performance and efficiency, a response to finding that as much as 75% of the life-cycle energy has been shown to be expended during the use phase. [92-95] However, concerns about material scarcity, processing impacts, and environmental opportunities of recycling highlight the need for more extensive study on the downstream end-of-life tradeoffs in a battery life cycle. [96-100]

Traditional recycling techniques involve smelting or leaching processes to recover valuable metals and materials that could potentially be used to synthesize new active materials. [101-103] Cathode materials are of particular interest, as they make a high percentage of the total battery
mass, and contain potentially critical metals (e.g. Li, Ni, Co). To reduce cell cost, lithium ion cathode chemistries with inexpensive elemental materials (e.g. Fe, Mn) are becoming more prevalent. However, the potential secondary value of these cathode materials recovered by traditional recycling techniques is also correspondingly reduced, thus decreasing the economic incentive for recovering these materials[104]. For example, the value of the recoverable LiFePO$_4$ materials through traditional recycling techniques is on the order of $0.75/lb whereas the cost of the cathode is more than an order of magnitude higher at $9.10/lb.[46] The EOL management of these cells must be proactively addressed to provide an economic incentive alongside the environmentally motivated policies such as battery disposal bans (e.g. 2012 NY state ban).

As opposed to traditional recycling methods, cathode refunomalization offers the potential for greater environmental and economic savings and may potentially improve the use phase performance.[105] As previously defined, refunomalization is the treatment of active materials in order to regain electrochemical performance at EOL.[105] The ability to systematically implement such a technology, however, depends on demonstration of both technical feasibility as well as environmental and economic benefits. It should be noted that a main requirement to enable a physical separation of a particular cathode in order to re-lithiate would be a controlled waste stream that contained the same cathode chemistry. This may not be practical for smaller batteries such as those for consumer electronics, but is potentially feasible for larger packs such as those beginning to be employed in electric vehicles and renewable energy storage. This work investigates the ability to regain the capacity of a lithium iron phosphate (LiFePO$_4$) cathode using a refunctionlization treatment though re-lithiation techniques. Re-lithiation techniques have been suggested in recent work as a possible EOL treatment for a different cathode
chemistry (LiMn$_2$O$_4$) using lithium carbonate, however, this is the first work demonstrating the recovered electrochemical performance data and the first for the LiFePO$_4$ chemistry.[106] Electrochemical and chemical lithiation of EOL LiFePO$_4$, from commercial cells, were compared to regain the performance of the cathode. The embodied energy of the refunctionalization process (lithiation) was compared LiFePO4 produced from virgin and recycled materials.

**ii. Methods**

Commercial lithium ion batteries in an 18650 form factor (18 mm x 65 mm) containing high power LiFePO$_4$ cathode chemistries were obtained by dismantling power tool battery packs to isolate individual cells. Cells were extracted from an 18V Dewalt XRP NANO phosphate pack by manually separating cells from the pack. These cells are manufactured by Sony Corporation with markings SE US18650FT and have a rated capacity of 1.1 Ah and a nominal voltage of 3.2V. Each power tool pack was purchased new from the Home Depot to obtain as-received cells that were most likely subjected to initial formation cycles. Individual 18650 cells were cycled galvanostatically using an Arbin BT-2000 from 3.6-2.0V at a 2C charge rate (2.2 A) and discharged at a 5C rate (5.5 A) in a 60°C convection oven to accelerate capacity fade. After 3000 cycles, the cells reached a capacity fade equal to 80% of the original measured capacity which was used as the end-of-life (EOL) state in this study.

The Sony 18650 cells were fully discharged to 0.5V and disassembled to obtain electrodes both directly after removal from the power tool pack (as-received cells) and after cycling to 80% of the original capacity (EOL cells). The cells were dismantled in an Argon filled glove box using a pipe cutter to remove the cells vented cap and a micro flush cutter to remove the rest of the can.
The 18650 “jelly-roll” was then unrolled and the cathode, anode, and separator were isolated. The cathode and anode from both the fresh and EOL cells were then tested in a 2032 coin cell vs. Li foil to determine the specific capacity of the electrodes. The cells were cycled at a C/10 rate (0.11A) from 3.6V to 2V with constant voltage step at 3.6V on the charge until the current dropped below 10% of the C/10 value with a 1.2M LiPF<sub>6</sub> EC:EMC electrolyte. Thermogravimetric analysis (TGA) was used to estimate the specific mass of materials within the composites. The active cathode LiFePO<sub>4</sub> weight percentage was found to be 82%. Fresh anodes were coated to pair with as-received and EOL cathode coatings to determine electrochemical performance in a full cell without the availability of excess lithium. The fresh anode was capacity matched to the cathode coatings. The slurry contained a mixture of 91.5(active graphitic carbons): 8 (Polyvinylidene fluoride): 0.5 (carbon black – Super P) w/w % in N-Methyl-2-pyrrolidone (NMP) and was coated using an adjustable blade coater onto 20 µm thick copper foil. The coating was dried on the coater at 80°C for 1 hour and was further dried in a vacuum oven at 100°C for 1 hour. The anode was then paired with the recovered fresh and EOL anode in a 2032 coin cell and electrochemically tested in the same manner as the previous coin cells.

The ability to recover the electrochemical performance of the EOL cathode was investigated through electrochemical and chemical lithiation techniques. EOL cathode coatings were electrochemically lithiated by cycling the cathode coating vs. pure lithium in a coin cell using the method stated previously for several cycles and then discharging the cell to fully lithiate the cathode. The coin cell was then disassembled using a coin cell disassembling tool (Hohsen) in an Argon filled glove box to obtain the “re-lithiated” cathode. The electrochemically lithiated
cathode was then paired vs. a fresh anode to compare to the fresh cathode in a coin cell and
electrochemically tested using the same method stated earlier.

*Chemical* lithiation of the EOL cathode was done by scraping the cathode coating from the
aluminum current collector and grinding the powder using a mortar and pestle. The ground EOL
cathode coating was placed in a 1M solution of lithium iodide (LiI) in acetonitrile and stirred for
20 hours to chemically lithiate the LiFePO_{4} cathode. The cathode materials were recovered
through vacuum filtration using a 0.1 µm polypropylene filter paper and rinsed with acetonitrile
to remove excess LiI. The recovered cathode materials were then dried under vacuum at 100 °C
for 1 hour and ground with a mortar and pestle. A composite was then cast using the recovered
materials by mixing in NMP and coating onto aluminum foil following the same method stated
earlier in casting the fresh anode. The chemically lithiated composite was then tested
electrochemically in a 2032 coin cell versus both Li/Li^{+} and a capacity matched fresh anode.

The as-received, EOL, and chemically lithiated cathode materials were characterized using
scanning electron microscopy (SEM) and x-ray diffraction (XRD). SEM was performed using a
field emission Hitachi S-900 microscope at 2kV. XRD measurements were taken on a D2 Phaser
benchtop XRD system (Bruker AXS, Germany) using Co Kα radiation (k=1.789 Å) scanning
between 2θ of 10° and 80°. All samples were prepared by uniform packing of material in sample
holders.

Cumulative energy demand (CED) was calculated to determine the environmental tradeoffs of
producing new virgin materials as compared to using recycled materials or a refunctionalized
cathode. CED includes all energy inputs across the life cycle of the materials, including both direct process electricity, as well as energy required to produce electricity and other raw materials. As a baseline, the CED was calculated for synthesis of LiFePO$_4$ from virgin materials using existing LiFePO$_4$ production modeling of a lab-scale hydrothermal production using EcoInvent inventory data and calculated using the CED method in SimaPro (Pre, The Netherlands) [94].

The CED of producing LiFePO$_4$ from recycled materials was modeled using intermediate physical recycling and re-synthesis of LiFePO$_4$ using a recycled lithium source. Intermediate physical recycling involves shredding and separation of the lithium containing components which are converted to lithium carbonate to synthesize new cathode materials. The recycled lithium carbonate is used to produce the lithium hydroxide precursor in the hydrothermal synthesis. Therefore, the CED for the lithium carbonate is equal to the intermediate recycling CED to recover the lithium carbonate which has been modeled in previous work, and eliminates upstream impacts from the production of virgin lithium carbonate[107]. The recycling of lithium carbonate was modeled using EcoInvent inventory data as well.

The CED to refunctionalize EOL LiFePO$_4$ cathode through chemical lithiation was modeled using direct physical recycling to recover the EOL cathode, and the energy and materials consumed in the chemical lithiation process. Direct physical recycling involves only shredding and filtering processes to isolate the EOL cathode material and has been modeled in previous work[107]. Chemical lithiation and refunctionalization energy impacts were modeled based on the relithiation of 1 kg of EOL LiFePO$_4$. The amount of lithium needed for relithiation of 1 kg of
EOL LiFePO$_4$ was calculated using the capacity loss of the EOL cathode and multiplying by lithium capacity (3860 mAh/g). Stoichiometric ratios were used to calculate the mass of LiI required, and the resulting mass of acetonitrile to make a one molar solution. LiI production CED was modeled from the reaction of lithium hydride with iodine in diethyl ether[108]. A solvent recovery CED of acetonitrile and the diethyl ether used in the LiI production were calculated following previously published procedures[109]. Direct measurements (Watts up? Pro ES meter) and nameplate equipment power consumption were used to model the energy required to stir, filter, and dry the material at the lab scale. Ecoinvent data and GaBi software were used to calculate the refunctionalization CED. In all cases, the energy consumption of the synthesis or refunctionalization process was modeled using U.S. medium voltage electricity mix.

iii. Results and Discussion

Commercial 18650 cells containing a lithium iron phosphate (LiFePO$_4$) cathode chemistry were obtained from a power tool pack shown in Figure 38 inset. Some of the individual cells were then subjected to accelerate cycling at 60°C at a 2C charge and 5C discharge rate to force a capacity fade in a reasonable amount of time. After 3000 cycles (approximately 3 months), the cycled cells had faded to 80% of the original measured capacity and were used as end-of-life (EOL) cells in this study. The cycling performance of one of the cells is demonstrated in Figure 38. This capacity fade is similar to recent work on LiFePO$_4$ cell cycling.[110]
Figure 38. The electrochemical cycling performance of an 18650 cell under accelerating testing conditions. (Inset) Pictures of partially disassembled power tool pack containing 18650s with LiFePO$_4$ cathode chemistry (Images taken by the author).

The EOL and an as-received (not cycled) cell from the pack were then fully discharged to 0.5V and disassembled to obtain the individual electrodes for testing versus lithium to determine the performance of the isolated electrodes. After disassembly of the cells, a possible failure mechanism is apparent when qualitatively evaluating the electrodes from the fresh cells. While the cathode is generally compressed and well adhered to the aluminum current collector, the anode coating from both cells easily delaminates from the copper current collector, and in some cases is adhered to the separator. The delamination can lead to a loss of contact between active
anode particles and the current collector, which will cause a reduction in capacity. Figure 39 demonstrates the lack of adhesion of the anode coating (a) and an intact cathode coating (b).

![Figure 39](image-url)

**Figure 39 a.** Anode demonstrating anode delamination from the copper current collector and adhesion to the separator. **b.** Cathode coating that is well adhered to aluminum current collector (Images taken by the author).

A bill of materials for each cell was taken to determine the materials available for recycling in each cell. A total mass was recorded before dismantling the cells and any loss in mass in the BOM accounting was assumed to be evaporated electrolyte. Three ½” punches from each electrode, in areas with adhered coatings, and the separator were massed and averaged before and after drying a vacuum oven at 100°C in order to determine the amount of electrolyte that was soaked into the electrodes and separator. A coating mass for the anode and cathode were found by averaging the mass of three ½” punches of the respective current collector in order to get a percentage of the electrode that was current collector compared to coating. The active material mass in the coatings was calculated using the specific capacity of the active material and the
capacity of the 18650 cell to determine an active mass percentage in the coating. The carbon conductive additive and PVDF binder were found through thermogravimetric analysis. Table 7 gives a breakdown of the BOMs by battery component, which shows a similar breakdown of materials in the cell with some small variations. Besides the steel casing, the active cathode materials are the highest individual material mass at 19-20% of the total cell mass. It should be noted that for this high power cell, the mass of the anode and cathode are similar with the anode actually weighing slightly more due to the heavy copper current collector. The data here further supports the energy density approach described in chapters 4, 5, and 6.
<table>
<thead>
<tr>
<th>BOM Summary</th>
<th>Sony 18650 (LiFePO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass (g)</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td></td>
</tr>
<tr>
<td>Active Cathode</td>
<td>7.34</td>
</tr>
<tr>
<td>Carbon Additives</td>
<td>0.92</td>
</tr>
<tr>
<td>PVDF Binder</td>
<td>0.92</td>
</tr>
<tr>
<td>Al Current Collector</td>
<td>1.98</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>11.16</strong></td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td></td>
</tr>
<tr>
<td>Active Anode</td>
<td>3.96</td>
</tr>
<tr>
<td>Carbon Additives</td>
<td>1.32</td>
</tr>
<tr>
<td>PVDF Binder</td>
<td>1.32</td>
</tr>
<tr>
<td>Cu Current Collector</td>
<td>5.30</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>11.89</strong></td>
</tr>
<tr>
<td><strong>Separator (PP or PE)</strong></td>
<td>1.90</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td></td>
</tr>
<tr>
<td>LiPF₆</td>
<td>0.55</td>
</tr>
<tr>
<td>Carbonate Solvents</td>
<td>3.65</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4.20</strong></td>
</tr>
<tr>
<td><strong>Packaging</strong></td>
<td></td>
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<tr>
<td>Steel Casing</td>
<td>8.51</td>
</tr>
<tr>
<td>Plastic Packaging (tape, gaskets)</td>
<td>0.77</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>9.28</strong></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>38.43</strong></td>
</tr>
</tbody>
</table>

*Table 7. Bill of material breakdown of Sony cells.*
A further breakdown of the BOMs was performed to obtain an elemental analysis of the materials in each cell. The mass of each element in the active cathode was calculated using the stochiometric ratio of elements in the cathode material. The results are shown below in Table 8 which provides information on amount of individual elements that could be extracted from each cell through traditional recycling techniques.

<table>
<thead>
<tr>
<th>BOM Summary</th>
<th>Sony 18650 (LiFePO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% of Mass (g) Total</td>
</tr>
<tr>
<td>Lithium</td>
<td>0.32 0.84</td>
</tr>
<tr>
<td>Iron</td>
<td>2.60 6.76</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>1.44 3.75</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.98 7.75</td>
</tr>
<tr>
<td>Aluminum</td>
<td>1.98 5.15</td>
</tr>
<tr>
<td>Copper</td>
<td>5.30 13.79</td>
</tr>
<tr>
<td>Steel</td>
<td>8.51 22.15</td>
</tr>
<tr>
<td>Carbon (active anode and conductive additives)</td>
<td>6.19 16.11</td>
</tr>
<tr>
<td>PVDF</td>
<td>2.24 5.82</td>
</tr>
<tr>
<td>LiPF6</td>
<td>0.55 1.43</td>
</tr>
<tr>
<td>Carbonate Solvents</td>
<td>3.65 9.50</td>
</tr>
<tr>
<td>Plastics (separator and packaging)</td>
<td>2.67 6.95</td>
</tr>
<tr>
<td>Total</td>
<td><strong>38.43 100.00</strong></td>
</tr>
</tbody>
</table>

Table 8. Elemental breakdown of the bill of materials for Sony and Sanyo 18650 cells.
The first cycle voltage curves for the as-received and EOL cathodes are shown in Figure 40(a). The first cycle charge capacity for the EOL LiFePO$_4$ cathode is significantly lower, 110 mAh/g, than the charge capacity for the as-received LiFePO$_4$ cathode, 157 mAh/g. However, the discharge capacity for the two cells is in the expected capacity range for LiFePO$_4$ of 150-155 mAh/g. During charge, lithium ions are being removed from the cathode structure; therefore, a lower charge capacity indicates a loss of lithium from the structure and is a main contributor to the full cell capacity fade. The increase in capacity upon discharge demonstrates that the LiFePO$_4$ structure may be able to re-lithiated electrochemically versus a lithium metal anode. The as-received cathode has a charge capacity much closer to that of the discharge capacity demonstrating that the as-received cathode has a fully lithiated LiFePO$_4$ structure.
Figure 40. (a) Voltage profiles for as-received and EOL LiFePO$_4$ cathodes and (b) x-ray diffraction (right) of as-received (black) and EOL (red) LiFePO$_4$ cathodes with reference peaks for LiFePO$_4$ (blue) and Li$_{0.05}$FePO$_4$ (green) (results are best case scenario).
The difference in crystal structure of the cathode was further investigated using x-ray diffraction (XRD). The as-received and EOL cathodes were scraped from the aluminum current collector and ground in order to take powder XRD measurements. The XRD spectra can be seen in Figure 40 (b) where both cathodes demonstrate the reference LiFePO₄ peaks shown in light blue. However, an increase in intensity and appearance of new peaks is observed for the EOL cathode. These peaks marked by a star in Figure 40b are indicative of a delithiated Li₀.₀₅FePO₄ phase (reference lines shown in green) within the EOL cathode. The XRD results further demonstrate that some of the LiFePO₄ within the EOL cathode has lost lithium from the structure due to cycling.

To test the performance of the as-received and EOL cathodes without the presence of excess lithium, a new anode was cast that was capacity matched to the cathodes and the electrodes were paired versus each other in a full cell. The voltage profiles for both the as-received and EOL cathodes versus the new anode can be found in Figure 41 (a) with capacity stated with respect to the cathode. The results again demonstrate that the EOL cathode lost lithium from some of the LiFePO₄ resulting in an initial capacity of 85 mAh/g compared to 132 mAh/g for the as-received cathode. It should be noted that the initial discharge capacity is a somewhat lower than expected for the as-received cathode due to the first cycle loss from formation of a SEI layer on the new anode which is consistent for all samples paired with a new anode. The cycling performance of these cells over 50 cycles is demonstrated in Figure 41 (b) which shows the significant loss in capacity of the EOL cathode.
Figure 41. (a) Voltage profiles and (b) cycling date for an as-received and EOL Sony cathode vs. a newly coated anode (results are best case scenario).
EOL cathode refunctionalization was investigated through electrochemical and chemical lithiation. As characterized in the previous section, the main capacity fade mechanism of the EOL cathode in this case is due to the loss of lithium due to cycling which caused lithium to be irreversibly lost. However, after removal from the 18650, the cycling results of the EOL cathode vs. lithium demonstrated the ability to re-lithiate the cathode electrochemically as the discharge capacity of the cell was found to be the same as the as-received cathode. Therefore, the ability to refunctionalize the EOL cathode through electrochemical lithiation was investigated by cycling the EOL cathode vs. lithium in a coin cell for multiple cycles and discharging the cell to fully lithiate the cathode. The cell was then disassembled and the electrochemically lithiated cathode coating was then paired vs. a capacity matched new anode. The first cycle voltage profiles comparing the as-received LiFePO$_4$ cathode and the electrochemically lithiated EOL cathode versus the new anode are shown in Figure 42 (a). The results demonstrate that the cathode capacity can be regained through electrochemical lithiation where the refunctionalized cathode had a similar charge and discharge capacity compared to the fresh cathode. The cycling performance was also found to be similar after 50 cycles as shown in Figure 42 (b) demonstrating that relithiated LiFePO$_4$ cathode can retain the capacity of the as-received cathode for several cycles.
Figure 42. (a) Voltage profiles and (b) cycling discharge capacity for an as-received cathode (black) and an electrochemically lithiated EOL cathode (blue) vs. a new anode (results are best case scenario).
Although electrochemical lithiation is demonstrated to refunctionalize the EOL cathode coating and to enable the reuse of the coating in a new cell, the process may not be scalable and relies on the cathode having sufficient mechanical adhesion to the current collector at EOL. A more scalable technique may be to remove the cathode coating from the current collector and use a solution based chemical lithiation. Therefore, chemical lithiation of the EOL cathode was investigated by scraping the cathode coating from the aluminum current collector, grinding to a powder and stirring in a one molar Lithium Iodide (LiI) solution in acetonitrile for 20 hours.

Immediately after addition of the cathode materials to the LiI solution, the color visibly changes from a light yellow solution to a brown solution due to the formation of Iodine in the solution. XRD was taken of the chemically lithiated cathode powder shown in Figure 43 which demonstrated the absence of de-lithiated peaks associated with delithiated LiFePO$_4$, peaks are starred, similar to that of the as-received LiFePO$_4$. 
Figure 43. XRD of as-received, EOL, and chemically lithiated LiFePO$_4$ cathode composites.

Scanning electron microscopy images were taken of as-received and chemically lithiated cathodes scrapped from the aluminum current collector and are shown in Figure 44. The as-received electrode is pictured on the left whereas the chemically lithiated cathode is on the right. The images do not show any qualitative differences between the two samples and the presence of the cathode particles as well as high aspect ratio conductive carbons (i.e. VGCF, MWCNTs) can be found in both images. This indicates that the conductive additive was not lost in the chemical lithiation and filtration process.
The chemically lithiated cathode powder was then cast by dispersing in N-Methyl-2-pyrrolidone (NMP) and coating onto an aluminum current collector. The coating was well-adhered to the current collector which indicates that the polymer binder in the cathode coating was retained through the chemical lithiation process as well. The chemically lithiated cathode was tested versus lithium and a capacity matched new anode and the voltage curves can be seen in Figure 45. The results demonstrate that the chemically lithiated cathode had a discharge capacity very close to that of the as-received sample for both cases. A larger first cycle loss was found when tested versus a graphitic anode due to a higher first cycle charge capacity for the chemically lithiated sample which may be due to excess lithium retained after the chemical lithiation process. However, the similar discharge capacity and material characterization demonstrate that both chemical and electrochemical lithiation are a promising new method to reuse active materials through material refunctionalization along with the conductive additives and binder.

**Figure 44.** Scanning electron microscopy (SEM) images of as-received (left) and chemically lithiated (right) LiFePO$_4$ cathode coatings scraped from Al current collector.
Figure 45. Voltage profiles for fresh and chemically lithiated EOL (purple) LiFePO₄ cathodes versus (a) lithium and (b) a capacity matched new anode (right) (results are best case scenario).
The economic and environmental benefit of LiFePO$_4$ refunctionalization compared to synthesis from virgin or traditionally recycled materials is owed to the ability to recapture valuable cathode materials before they are returned to a low-value elemental level. Of course, the cost and energy intensity of the recovery and isolation of the cathode material or coating and refunctionalization process must be taken into account as well. To quantify potential tradeoffs in recovery or recycling methods, cumulative energy demand (CED) was calculated for each potential EOL pathway and compared to the initial impacts of producing the virgin raw materials. Intermediate recycling is modeled for the production of LiFePO$_4$ from a recycled lithium source. A lithium carbonate source is recovered through shredding and precipitation and the energy of the process has been modeled in previous work[106]. These results (Figure 46) demonstrate a reduction of approximately 10% in embodied energy when cathode materials are recycled and then used in the synthesis of a new cathode, as compared to the all virgin raw material baseline. In the case of refunctionalization, physical separation has a higher CED than traditional recycling due to the energy to recover all 1kg of EOL LiFePO$_4$ as compared to the allocation of energy to recover just the lithium source. However, the net CED is reduced by 50% due to the complete elimination of any virgin material demand and a re-lithiation process that uses low temperature and energy. It should be noted as well that the chemical lithiation processes were modeled at the lab scale and further CED reduction may be possible with scale up. While results shown here focus on the cathode, benefits of recycling and refunctionalization would likely extend to the entire cell, which could be recycled for material recover (e.g. steel or aluminum from casings) or remanufactured for reuse (e.g. housing the refunctionalized cathode).
Figure 46. Embodied energy for LiFePO$_4$ produced through synthesis using virgin materials (grey) and recycled materials (blue), and chemical lithiation of EOL LiFePO$_4$ (purple) (results are best case scenario).
Summary and Acknowledgements

Commercial LiFePO₄ containing cathodes were cycled to an EOL state and recovered from the cells. Coin cell testing and x-ray diffraction revealed that the main fade mechanism is caused by a loss of lithium with cycling. The ability to refunctionalize the EOL cathode to as-received performance was demonstrated using electrochemical and chemical lithiation. These results offer a new method to reuse lithium ion cathode materials at EOL which can reduce cost and energy of synthesizing new cathode materials. The potential environmental benefit of the chemical lithiation process was confirmed by calculations of cumulative energy demand up to 50% lower than that of synthesis from virgin materials.
CONCLUSION AND MAJOR CONTRIBUTIONS

This dissertation contained significant contributions to the understanding of nanomaterial impacts throughout a lithium ion battery life cycle. At the beginning of life, the embodied energy of laser vaporization synthesis and purification was quantified for the first time. The embodied energy of the lab scale process was slightly higher than other larger scale methods previous published. However, a significant reduction in embodied energy is possible with scaling of the process and efficiency improvements. The establishment of SWCNT production process CED within a life cycle framework is important to establish a baseline embodied energy and provide avenues for efficiency improvements. Ideally, the embodied energy of SWCNT production would be compared to benefits in the use phase to determine the ultimate environmental impact, and is an opportunity for future work. However, SWCNT production may still be at too early of a stage to obtain a truly accurate cost-benefit analysis.

The use phase performance of lithium ion batteries was enhanced by incorporating carbon nanotubes into various electrode designs. To fully utilize the properties of SWCNTs as a conductive additive, a dispersion technique was developed to integrate SWCNTs through the electrode composite where SWCNTs could entangle active particles and enable long range connectivity forming an enhanced percolation network. As a cathode conductive additive, a low weight percent of SWCNTs (1%) increased voltage and capacity retention at faster discharge rates with 3x the capacity retention at a 10C rate compared to a larger weight percentage of traditional additives (4%). The effect of CNT conductive additives on thermal stability was measured for the first time using DSC. The results demonstrated that, as an additive, the exothermic energy released for a typical metal oxide cathode decreased by 40% upon overcharge.
due to the incorporation of the high thermally conductive SWCNTs. Similar rate and thermal stability improvements were determined when using SWCNTs as an anode additive and demonstrated the ability to engineer electrodes to improve overall battery safety.

Energy density improvements were also discovered through the thickening of cathode composites and the use of CNT supports. The increase of cathode areal loading (thickness) can increase overall battery energy density by 50% by simultaneously increasing active material mass and decreasing the relative mass of the metallic current collector. The results demonstrated that SWCNT additives were necessary to provide enough electronic conduction and composite mechanical stability. The rate performance of higher loading composites was improved with the use of a higher SWCNT additive loading (2%) which achieved equivalent capacities up to a C/2 rate enabling higher energy density designs. The use of commercial CNT papers as replacements to heavy metal current collector composites for traditional composites was optimized through purification of the CNT sheet. The results demonstrated equivalent capacity and rate performance to metallic current collectors which can ultimately improve battery energy densities by 5-30%. CNT supports were utilized in next generation anode designs that incorporated high capacity Si and Ge. The electrodes were measured to have high capacities and the thermal stability of the free-standing anode designs and this was measured for the first time. The results demonstrated that coating of electrodes with Si decreased surface area which improved first cycle coulombic efficiencies and improved thermal stability. As the surface area of the electrodes was lowered, the temperature at which the reaction occurred was increased and the exothermic energy and intensity of the reaction were decreased. A thermal stability plot was developed that summarized the DSC data for electrodes utilizing CNTs by comparing
exothermic energy released to the intensity or thermal power of the reaction. The plots demonstrated a dependence on thermal conductivity, when SWCNTs are incorporated at a low weight percentage as an additive, and surface area, when CNTs are utilized as a free-standing support. This plot demonstrates the novel ability to engineer electrodes to control thermal stability. The impact of this work on battery energy density is summarized in Figure 47 for an 18650 cell. The use of SWCNT additives to thicken cathode composites and replacement of copper current collectors with CNTs was demonstrated in this work and both increase energy density by around 60%. The combination of high capacity Si and low weight CNT current collector can double the energy density of an 18650 cell. The improvement in energy density as well as safety of lithium ion batteries can ultimately improve device adoption. Increased electric vehicle adoption will lead to reduced fossil fuel dependence and lower emissions as discussed previously. This work demonstrates energy, power, and thermal stability improvements, but did not thoroughly investigate cycleability. An opportunity for future work exists in determining the effect of CNTs on battery cycle life.
Figure 47. Modeling of energy density improvements for anode technologies demonstrated in this work in an 18650 form factor versus an NCA cathode. (Modeling and figure were created by Dr. Michael Forney)
A novel EOL management pathway was developed for lithium ion active cathode materials. This pathway is defined as refunctionalization which treats cathode active materials at EOL to regain the original electrochemical performance. The refunctionalization of LiFePO$_4$ commercial cathodes at EOL was demonstrated through electrochemical and chemical techniques. Refunctionalization allows for recovery of the cathode at a higher value state, and could have a higher economic value; especially in the case of cathode materials like LiFePO$_4$ which contain lower value elements. The refunctionalized LiFePO$_4$ cathode recovered to the original capacity and crystal structure, as measured by XRD, compared to as-received LiFePO$_4$. The embodied energy of LiFePO$_4$ obtained through refunctionalization was compared to LiFePO$_4$ synthesized from recycled and virgin starting materials. The refunctionalization embodied energy was demonstrated to be around 50% lower than cathode synthesized from virgin and recycled materials, respectively. Refunctionalization has the potential to make cathode materials more valuable at the EOL and make recovery at EOL economical, even for cathodes containing low value elements. At the same time, the environmental impact can be reduced which makes refunctionalization a revolutionary EOL pathway. Future research opportunities exist in demonstrating the scalability of the process, and determining the ultimate economics and cost-benefits of cathode refunctionalization.
A summary of the significant contributions is given below:

1. Quantified the embodied energy of laser vaporization synthesis of single wall carbon nanotubes and compared to other synthesis methods.
2. Developed dispersion techniques to advance the use of novel CNTs additives towards power and energy density.
3. Demonstrated an improved thermal stability of battery electrodes through the use of SWCNT additives.
4. Contributed significantly to improved energy density through higher loading composites with SWCNT additives and free-standing electrode technology which can exceed traditional technologies energy density by 50%.
5. Developed thermal stability plot to compare traditional electrodes to new anodes incorporating high capacity Si and Ge with SWCNTs.
6. Contributed to the EOL studies of battery materials and was the first to demonstrate that refunctionalization is a viable pathway to manage active cathode materials at EOL.
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