ABSTRACT

HO, DAVID NAN. A Silicon-Impregnated Carbon Nanotube Mat as a Lithium-Ion Cell Anode. (Under the direction of Dr. Peter S. Fedkiw and Dr. Yuntian Zhu).

Silicon is a widely-researched lithium ion (Li-Ion) battery anode material due to its high theoretical energy density of 4200 mAh g^{-1} , more than 10 times the specific capacity of conventional graphitic materials. However, silicon degrades rapidly as a lithium-storage material due to the volumetric changes that occur during cycling; these effects are well-documented and necessitate the use of complicated or costly methods to ameliorate capacity loss. In lieu of these convoluted workarounds, this study presents a potential, novel silicon anode fabrication technique.

In this original method, anode discs were fabricated by winding a carbon nanotube (CNT) felt and infiltrating it in-situ with an aqueous solution containing silicon nanoparticles and a hydroxypropyl guar binder. The resulting infiltrated felts were processed and constructed into coin cells and evaluated compared to conventional silicon-carbon black anodes.

Samples had a large initial reversible capacity and promising rate capability performance. It is likely that the conductive CNT structure improves charge transfer properties while lessening the effects of volumetric expansion during lithiation. While there remains further work to be done, the results demonstrate that this novel anode fabrication method is viable and can be explored for further optimization.

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A Silicon-Impregnated Carbon Nanotube Mat as a Lithium-ion Cell Anode

by

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DEDICATION

“Somewhere, something incredible is waiting to be known.”

~ Carl Sagan

BIOGRAPHY

David Ho was born in Brooklyn, NY in 1989. Shortly after, he moved to NJ in 1990 and then down to Cary, NC in 1996. He attended Green Hope High School where he discovered his lifelong passion for the environment and engineering. He then attended and graduated from Cornell University in 2011 with a B.Sc. in Materials Science and Engineering. David then moved to Schenectady, NY after Starfire Systems, Inc. hired him in October 2011. He left the company in August 2014 when he decided to pursue graduate studies. He enrolled in the Non-Degree Studies program at North Carolina State University while applying to various graduate programs and working as a Visiting Scholar in the Fedkiw Research Group at NCSU with Salvatore Luiso. David was accepted into the Master's program in the Materials Science and Engineering Department at NCSU on May 2015. David attained joint membership in the Fedkiw and Zhu Research Groups for his thesis.

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CHAPTER 1. A NOVEL LITHIUM ION CELL ANODE

1. INTRODUCTION

1.1. Lithium Ion Batteries Background

Ever since their commercialization in 1991, lithium ion batteries (LIBs) have had an increasing presence in consumer devices, from personal electronics to the next generation of electric vehicles. Their combination of high cell voltage, high specific energy (also termed energy density), adaptability and high efficiency make LIBs excellent energy storage devices. Considering the wide applicability of LIBs, there are three primary metrics used to evaluate lithium ion battery performance: specific capacity, energy density and power density. Specific capacity, measured in mAh g^{-1} , denotes the total amount of charge a battery can store per unit mass. Energy density and power density figures both can be reported on gravimetric and volumetric bases. Energy density is measured in Wh kg^{-1} or Wh l^{-1} and denotes the amount of energy available to perform work; high energy density is useful in applications with long operating times such as cell phones. Power density is measured in W kg^{-1} or W l^{-1} and it's used to indicate the quality of electric current provided; high power density is useful for systems with high power drain such as power tools or electric vehicles with quick acceleration.

Figure 1.1: Ragone plot comparing different battery chemistries relative to their respective specific energy and specific power densities [1].

Energy and power densities are typically juxtaposed as a trade-off and are typically charted in a Ragone plot comparing them to other chemistries as shown in **Figure 1.1** ^[1]. Typical LIBs have an energy density of 250 Wh kg⁻¹ as shown in **Figure 1.1**. Nickel metal hydride batteries are the closest performing commercial battery, producing an energy density of about 100 Wh g⁻¹ ^[2], less than one half the energy density of LIBs. However, despite the commanding lead LIBs have over other battery chemistries, market impetus has pushed for larger capacities, larger energy densities, and larger power densities.

1.1.1. Operating Principles

LIBs consist of three primary components: the anode (negative electrode), the cathode (positive electrode), and the electrolyte.

Figure 1.2: Diagram illustrating the discharge process in typical LIB operation [3].

During battery discharge, the lithium oxidizes at the anode and de-intercalates its carbon host as shown in **Figure 1.2** ^[3]; the lithium is then transported through an ionically conductive electrolyte where they then intercalate in the cathode. A polymer separator placed between the electrodes prevents a short circuit while electrons travel through an external circuit and perform work. Essentially, the anode serves as a lithium source and the cathode serves as a lithium sink during discharge. During battery charge, the process reverses itself. By general definition, anodes undergo oxidation and cathodes undergo reduction, but because both electrodes undergo oxidation and reduction reactions depending on the battery's state of operation, the electrode designations are fixed for a battery in a state of discharge.

Most modern commercial anodes contain graphite and commercial cathodes are most commonly lithium metal oxides. Lithium-containing salts such as lithium hexafluorophosphate (LiPF₆) or lithium bis(oxalato)borate (LiBOB) are used as electrolytes; they are dissolved in cyclic carbonate solvents like ethylene carbonate (EC), ethylmethyl carbonate (EMC), or dimethyl carbonate (DMC) and mixed with additives

such as vinylene carbonate (VC) or fluoroethylene carbonate (FEC) to improve cycling performance. Binders such as polyvinylidene fluoride (PVDF) ensure electrode mechanical robustness, facilitate lithium ion conduction, and maintain good ohmic contact between electroactive materials and conductive additive elements.

Figure 1.3A: Structure of un lithiated graphite and **3B:** Structure of lithiated graphite [5].

During cycling, an inert, electrically insulating and ionically conductive sheath forms around the active material. This layer is termed the solid electrolyte interphase (SEI) and the phenomenon is inherent in all LIBs. During the first few charge/discharge cycles, lithium irreversibly reacts with various battery components such as the electrolyte and the active material. SEI formation is detrimental in that it results in an irreversible capacity loss from lithium consumption, but it is beneficial in that the SEI acts as a passivating layer, shielding the active material from further reactions. As the anode cycles, the active material typically experiences volume change during lithium intercalation and de-intercalation. For example, graphite can swell up to 11% ^[4] when lithiated compared to its un lithiated state as shown in **Figure 1.3A** and **B**. Cyclic charge/discharge of a cell induces stress gradients in the SEI and can cause fracture, exposing the active material's surface for lithium to further react with. New SEI then forms on the unprotected surface, consuming more lithium.

In graphite-based anodes, this phenomenon is minimal due to the low amount of volumetric expansion that graphite experiences. However, other potential charge storage materials such as silicon can expand up to 300% during lithiation ^[6]. This extreme swelling behavior not only pulverizes the SEI layer, it can also result in the bifurcation of the local silicon structure. If sufficiently severe, the active material can become electronically isolated from the conductive matrix and significantly reduce cell capacity.

1.1.2. Theoretical Background

As discussed earlier, LIB anodes physically store lithium ions for cycling. A typical graphitic anode half-cell discharge reaction is shown below:

Assuming constant temperature and pressure, an anode's potential can be calculated via the thermodynamic equation for Gibbs Free Energy:

$$\Delta G^\circ = -nFE^\circ \quad \text{Equation 1.1}$$

where ΔG° is the Standard Gibbs Free Energy, n is the number of electrons transferred in the redox reaction, F is Faraday's constant, and E° is the standard electrode potential of the reaction. Reactions with a $\Delta G^\circ > 0$ are defined as an electrolytic cell; these reactions do not happen spontaneously and must be induced via an external driving force. If a reaction has a $\Delta G^\circ < 0$, it is defined as a galvanic cell and they occur spontaneously. For example, battery anodes are classified as a galvanic cell during discharge and as an electrolytic cell during charge.

Equation 1.1 assumes the system is in thermodynamic equilibrium and thus at a constant state. While at equilibrium, it is possible to derive electrode potential as a function of concentration through the Gibbs Free Energy standard state equation:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{a_R}{a_O} \right) \quad \text{Equation 1.2}$$

where R is the gas constant, T is the temperature, a_R is the activity of the reaction product and a_O is the activity of the reactant. When **Equation 1.1** is substituted into **Equation 1.2**, the equation becomes:

$$-nFE = -nFE^\circ + RT \ln \left(\frac{a_R}{a_O} \right)$$

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{a_R}{a_O} \right) \quad \text{where } \frac{RT}{F} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} * 298 \text{ K}}{96485.3 \text{ C mol}^{-1}} = 0.0257 \frac{\text{J}}{\text{C}}$$

$$E = E^\circ - \frac{0.0257}{n} \ln \left(\frac{a_R}{a_O} \right) \quad (\text{at } T = 298 \text{ K}) \quad \text{Equation 1.3}$$

Equation 1.3 is known the Nernst Equation and it is widely used to relate the potential of an electrochemical cell to its standard electrode potential and the activities of its reactant and product.

However, during charge and discharge, chemical, electronic, and thermal effects occur simultaneously so the system is no longer at equilibrium. As such, electrode kinetics and its limiting factors must be considered; four primary factors contribute to a redox reaction rate: 1) Charge transfer at the electrode-electrolyte interface, 2) Electrode surface reactions such as adsorption and desorption, 3) Mass transfer effects such as diffusion, migration and convection, and 4) Chemical reactions occurring before/after the redox reaction.

1.2. Current Technology

Standard LIB anodes are fabricated in roll-to-roll processes where a slurry of active material, conductive additives, and binder are cast onto a conductive substrate such as copper and dried. Most LIB anodes today consist of various forms of carbon, most commonly graphitic carbon.

Figure 1.4A: ABAB stacking pattern of unlithiated graphite and **4B:** AAAA stacking pattern of lithiated graphite [5].

Graphite is typically ordered in an AB stacking pattern with offset graphene planes as shown in **Figure 1.4A**. When lithium intercalates in between the basal planes, the graphene planes align to accommodate the lithium ion and the graphite assumes a AA configuration as shown in **Figure 1.4B** and **Figure 1.5** [7].

Figure 1.5: Lithium storage sites in graphite basal planes [7].

Graphite can store one lithium ion per six carbon atoms, forming LiC_6 . Crystalline graphite has a theoretical capacity of 372 mAh g^{-1} and most commercial graphites have 320-360

mAh g⁻¹ capacity [8]. Methods such as ball-milling graphite or depositing a layer of amorphous carbon onto graphite's surface can increase its capacity to as high as 900 mAh g⁻¹. This increase in capacity is tied to an introduction of defects such as edge sites and vacancies which provide adsorption sites for the lithium [9–12]. **Figure 1.6** charts the specific capacity of conventional anode materials with higher capacity materials such as other Group 14 elements. Silicon (3600 mAh g⁻¹), tin (1000 mAh g⁻¹), and germanium (1500 mAh g⁻¹) are all being investigated as possible LIB anode materials [13].

Figure 1.6: Voltage versus capacity of various LIB cathodes and anodes [13].

Table 1.1: Nitta *et al.* outlined six primary strategies for enhancing LIB performance ^[14]

Strategy 1	Dimension Reduction	Through feature size reduction, it's possible to increase active material reactivity through increased surface area. In addition, it's possible to relieve the structural stresses seen in active materials that experience volumetric expansion during lithiation.
Strategy 2	Morphology Control	Control of a material's morphology can apply to both electrodes and separators. By tailoring morphology, one can enable faster mass and charge transport through said components.
Strategy 3	Doping and Functionalization	Doping and functionalizing promising materials can impart improved properties such as faster charge transport or improved thermal or chemical stability.
Strategy 4	Composite Formation	Combining an active material with structural and conductive media can produce a multi-functional material.
Strategy 5	Coating and Encapsulation	Inherent degradation mechanisms in LIBs can be prevented via proper coatings and encapsulation.
Strategy 6	Electrolyte Modification	Due to the electrolyte's significant role in SEI formation, it is possible to affect SEI properties to produce favorable properties via electrolyte additives

This thesis will focus on Strategies 4, 5 and 6 by suggesting a new method of fabricating a silicon-CNT felt composite (Strategy 4) with a novel binder (Strategy 5) and an electrolyte additive (Strategy 6).

1.2.1. Role of Carbon in Lithium Ion Batteries

Carbon can play two roles in LIBs. First, as stated before, carbonaceous materials such as graphite can serve as lithium hosts; second, they can also serve as conductive additives. The sp^2 -hybridized orbitals found in graphite, graphene and carbon nanotubes (CNTs) serve as excellent conductive pathways for electrons.

1.2.1.1. Carbonaceous Materials as Lithium Hosts

As stated before, it's possible to modify carbon to increase its specific capacity beyond the theoretical 372 mAh g^{-1} figure for graphite by inducing defects. As shown in **Figure 1.7** ^[15], it's not only possible for lithium to store in graphene basal planes, it's also possible for lithium to form Li_2 and store it in interstitial sites between lithium ions ^[16]. **Figure 1.7c** and **d** illustrate other storage mechanisms involving void occupation and adsorption.

Figure 1.7: Lithium storage mechanisms in a) graphite. b) Li_2 covalent molecules inhabiting basal plane interstitial sites. c) Li^+ storage in voids and cavities. d) Dahn's model of Li adsorption onto graphene [15].

CNTs can make excellent lithium hosts depending on their chirality and diameter; they are much more robust than graphite and are not susceptible to solvent-based exfoliation like graphite ^[13]. Single wall carbon nanotubes (SWCNTs) perform better than their multiwall carbon nanotube (MWCNT) counterparts. Pristine SWCNTs can form up to a $\text{Li}_{1.6}\text{C}_6$ intercalation density with lithium ions arranging inside CNT tube bundles as shown in **Figure 1.8**.

Figure 1.8: Unit cell of CNT tube bundles with lithium (white dots) inhabiting interstitial sites [17].

Ball-milling SWCNTs was found to further increase intercalation density to a $\text{Li}_{2.7}\text{C}_6$ configuration ^[17]. This increase in intercalation density translates to a theoretical capacity greater than 1000 mAh g^{-1} . In addition, tube ends typically occupy a lot of free volume that can serve as lithium storage sites. Consequently, shorter CNTs exhibit better reversibility than longer CNTs. Long CNTs ($1 \text{ }\mu\text{m}$ long) saw a specific capacity reduction from 811 to

480 mAh g⁻¹. Comparatively, short CNTs (200 nm long) saw a specific capacity reduction from 593 to 577 mAh g⁻¹ after their first cycle [18].

1.2.1.2. Carbonaceous Materials as Conductive Additives

One of the most common conductive additive used in LIBs is carbon black due to its relatively low cost, tailorable surface area, and good conductivity ranging from 2.520 S cm⁻¹ [19]. CNTs can also be used as conductive additives; they exhibit excellent axial electric conductivity on the order of hundreds of S cm⁻¹ depending on their configuration (i.e., aligned CNT mats, CNT powders, surface functionalized CNTs, etc.) [20–22] and when arranged into a mat configuration as shown in **Figure 1.9** and **Figure 1.10** [23,24], their through-plane conductivity is on the same order as that of carbon black [25].

CNTs can be utilized in a variety of other ways from electrospinning to buckypaper fabrication. Caution must be taken when using SWCNTs however; chirality becomes nontrivial and SWCNT configuration can affect conductivity. *Arm-chair* configuration SWCNTs always have metallic conductive properties while *zig-zag* SWCNTs can be both metallic or semiconductive in nature depending on the chirality [26].

Figure 1.9: Drawing process of CNT felt mat [23].

Figure 1.10: Diagram of CNT felt precursor forest drawn into CNT felt mat [24].

1.2.2. Silicon Anodes

Silicon is being investigated as a potential charge storage material. It has been found that lithium forms intermetallic complexes with silicon at ambient conditions (Li_xSi_y where $\frac{x}{y} < 4$). While the theoretical specific capacity of silicon has been determined to be 4200 mAh g^{-1} , this corresponds to the $\text{Li}_{4.4}\text{Si}$ intermetallic phase that is difficult to

achieve due to kinetic limitations at standard temperatures and pressures. Several groups have confirmed silicon's practical specific capacity to be about 3600 mAh g^{-1} [27,28].

Figure 1.11: The transition from a (a) single-phase crSi particle to a two-phase microstructure during lithiation and (b) its transition during delithiation to an a-Si particle [6].

As mentioned earlier, silicon experiences volumetric expansion and contraction during lithiation and de-lithiation. When alloyed, lithium and silicon form a new amorphous Li_xSi (a- Li_xSi) phase in conjunction with the silicon phase; **Figure 1.11** illustrates the resulting two-phase structure. This process induces internal stresses in the a- Li_xSi phase and along the phase boundary which will inevitably lead to fracture during cycling; this cyclic process in turn causes recurrent SEI formation, resulting in a very sharp capacity drop within the first few cycles. In addition, silicon is a poor conductor so it must be coupled with conductive additives to bolster the charge transfer process at the electrode-electrolyte interface. Thus, many research groups are trying to analyze and understand the silicon lithiation process to determine major failure mechanisms with the aim of controlling these

processes. Particle size has been correlated to fracture probability. It has been demonstrated that there exists a critical particle size, ~ 150 nm, below which particles will not fracture during the first lithiation cycle ^[29]. This behavior is also present in silicon nanowires (SiNWs) of differing diameters; Chan et al. reported SiNWs remaining intact during lithiation (89 nm diameter unlithiated) ^[30] while Liu et al. reported anisotropic swelling with larger SiNWs (216 nm diameter unlithiated) ^[31]. Both studies grew nanowires in the $\langle 112 \rangle$ directions. It was reported that above a certain size threshold, the underlying cause of fracture was the buildup of a large tensile hoop stress caused by growth of the two-phase interface. This failure mechanism has been reported in other studies ^[32].

Another popular research approach is to develop different anode structures to alleviate the electrode damage caused by silicon expansion as well as to provide adequate charge transfer properties so the electrode has good rate capability. One widespread method involves combining silicon with a carbon-based support structure, usually graphite or CNTs; this can be used in conjunction with an amorphous carbon coating to enhance rate capability.

Figure 1.12: a) SEM image of Si/CNT composite and its b) TEM counterpart. Note the large amount of void space [33].

As shown in **Figure 1.12**, CNTs grown on SiNPs contain a significant amount of void space that can act as “buffering” layers ^[33]. Depositing a layer of amorphous carbon has been shown to increase cycling performance by as much as 200% ^[34]. Other ventures have investigated electrospinning Si-carbon nanofiber composites ^[35,36], CVD deposition of a-Si and a-carbon onto buckypaper ^[24] and casting SiNP/graphene composites ^[37].

1.2.3. Binding Agents

Binding agents have several roles in an electrode. They must provide adequate ionic conductivity through electrolyte uptake, maintain ohmic contact between active and conductive materials and preserve electrode structural integrity. Polyvinylidene fluoride (PVDF) is the common binder used in carbon anodes; however, PVDF fares poorly in silicon anodes. Si-PVDF anodes see a drastic drop in capacity during the first few cycles due to excessive SEI formation around the silicon ^[38]. Other polymer binders such as carboxymethyl cellulose (CMC), sodium alginate (SA), and polyethylene oxide (PEO) have been studied as potential binders for silicon anodes. Recent studies have investigated guar gum as a possible candidate and it’s been shown to outperform CMC and PVDF ^[39,40]. It has been hypothesized that –OH and –COOH functional groups are vital for binders to hydrogen bond to the native oxide layer that forms on silicon ^[41].

1.2.4. Electrolyte Additives

SEI properties significantly affect a silicon anode’s cycling performance. If the SEI layer is too brittle, it cannot elastically deform and thus fractures during cycling; this in turn causes additional lithium consumption and irreversible capacity loss. Compounds such as

FEC and VC are added to electrolyte solutions to intentionally react with cell components such as solvent and electrolyte and impart beneficial properties to the SEI, therefore stabilizing cycling behavior. There are other types of additives that serve different purposes such as stabilizing the LiPF_6 electrolyte and protecting the cathode; this paper will primarily focus on SEI modifiers, specifically polymerizable additives.

Figure 1.13: EC and lithium reaction mechanisms with intermediary radical anion [42].

During cycling, electrons produced from the lithium oxidation can undergo ring-opening reactions with cyclic carbonate solvents such as EC as shown in **Figure 1.13**. Based on lithium-ion cell chemistry, EC has two possible degradation paths: mechanism I converts an intermediary radical anion (RA) product into a Li_2CO_3 -abundant SEI with gaseous products and mechanism II transforms the intermediary RA into an electrolyte-insoluble species [42].

Figure 1.14: General reaction for electrochemically induced polymerization [42].

Figure 1.15: FEC polymerization reaction [43].

FEC and VC fall into the category of polymerizable additives because they undergo electrochemically induced polymerization during cycling. **Figure 1.14** illustrates the general mechanism by which VC polymerizes. FEC polymerizes via a similar reaction as shown in **Figure 1.15** ^[43]. The resulting polymer lends elasticity to the SEI and helps it cope with the volumetric change during cycling. While improving the cycleability of lithium metal is irrelevant to LIB operation, it is beneficial to lithium half cells where lithium foil is used as both a counter electrode and reference electrode.

2. HYPOTHESIS

Due to the better through-plane conductivity of CNT felt compared to carbon black and the favorable properties of guar gum as a potential silicon anode binder, we hypothesize that a CNT felt impregnated with silicon nanoparticles and a guar gum binder with an FEC electrolyte additive will yield a more environmentally friendly lithium ion cell anode with better cycling performance and rate capability as compared to conventional slurry-casted silicon/carbon black anodes.

3. OPERATIONAL STATEMENT

To produce the anode, a CNT array (as received) was wound onto a TeflonTM sheet on a rotating mandrel. The CNT felt was then infiltrated during the winding process with an aqueous solution containing the active material and binder. The initial felt composition was set as 55 wt% silicon, 35 wt% CNTs, and 10 wt% guar gum binder. Different compositions were studied to assess the effect of silicon content on cycling performance. After the infiltrated CNT felt was dried and consolidated, they were fabricated into a lithium half-cell with a lithium foil counter electrode and modified BASF SelectilyteTM LP-50 electrolyte (1 M LiPF₆ salt dissolved in 1:1 solution of EC:EMC) containing 20 wt% FEC. The anodes were characterized via galvanostatic cycling with potential limitation (GCPL) and electrochemical impedance spectroscopy (EIS). The anodes were also physically characterized via thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

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CHAPTER 2. EQUIPMENT AND EXPERIMENTS

1. PRIOR PROCESSING TECHNIQUES

As described in Chapter 1, this thesis centers around developing a process to infiltrate a CNT felt with a solution containing silicon nanoparticles and a polymeric binder in situ during fabrication by winding onto a mandrel. This section details the prior work done with these materials and processing changes made to adapt these different technologies for the purpose at hand.

The CNTs utilized in this study were grown by Ozkan Yildiz in the Bradford Research Group at North Carolina State University. They were characterized as multiwall CNTs with outside diameters of approximately 30 nm ^[1]; the number of walls weren't measured but CNTs grown in similar conditions reported 2-4 walls ^[2]. As measured by Bradford et al., the through-plane conductivity of bare CNT felt is 42 S cm⁻¹ ^[2] as compared to a conductivity of approximately 2.5-20 S cm⁻¹ for carbon black ^[3].

Figure 2.1: Polyvinyl alcohol (PVA) infiltration of CNT array felt [4].

There has been prior work done with infiltrating the carbon nanotube arrays produced by the Bradford group at North Carolina State University. The most common processing method involves winding the CNTs onto a mandrel and using a spray gun to infiltrate the felt in situ as shown in **Figure 2.1**. However, the process is difficult to control accurately because the spray gun used was a simple aerosol device powered by compressed air, resulting in an imprecise solution spray rate. To achieve the precise compositions planned for this study, a more precise method of infiltration was needed.

Silicon nanoparticles have been incorporated into LIB anodes before with CNTs as a conductive support. Whether electrospinning Si-CNT solutions for impregnated carbon nanofibers or mixing Si-CNT slurries to cast a film, good silicon dispersion must be achieved to maximize available silicon surface area. First and foremost, SiNP agglomerates can reduce anode capacity by electrochemically isolating active material. Second, charge transfer is the rate-limiting factor in silicon-containing anodes so maximizing surface area can increase available redox reaction sites. To achieve good Si-CNT dispersion, toxic or harsh solvents such as tetrahydrofuran (THF) or dimethylformamide (DMF) are commonly used to disperse CNTs ^[5-7]. Since this thesis seeks to produce a relatively low-cost LIB anode, utilizing safer dispersants and low-environmentally impacting chemicals would minimize scalability costs through hazardous-waste reduction and incurring less safety regulations. More popular and safer solvents such as isopropyl alcohol and ethanol will be investigated instead.

There hasn't been much work done with guar gum as a binder for silicon-containing anodes. Because guar gum is water soluble and insoluble in most organic solvents, it's

typically mixed with active material and conductive additives in a water-based slurry and then cast onto a current collector ^[6,8].

2. ADOPTED PROCESSING TECHNIQUES

While guar gum is water-soluble only, silicon nanoparticles and carbon nanotubes are inherently hydrophobic so a balance must be struck between the different infiltration solution components. Initial work in this thesis studied the solubility of guar gum in various organic solvents including ethylene glycol, methanol, ethanol and isopropyl alcohol. It was found that guar gum precipitated in aqueous solutions of more than 10 vol% organic solvent content. Guar gum was eventually deemed incompatible when infiltration solutions did not adequately disperse the SiNPs nor were they able to sufficiently wet the CNT felt.

Figure 2.2: Molecular structure of guar gum polymer chain [8].

Figure 2.3: Structure of hydroxypropyl guar gum [9].

Consequently, the decision was made to replace the guar gum binder with a functionalized version called hydroxypropyl guar (HPG) which has increased alcohol solubility compared to native guar gum. HPG is prepared from guar gum via irreversible alkylation with propylene oxide in the presence of an alkaline catalyst ^[9], partially substituting hydroxypropyl groups (–CH₂CH(OH)CH₃) onto existing hydroxide sites seen in **Figure 2.2** and **Figure 2.3**. These new hydroxypropyl groups impart organic solvent solubility and the resulting polymer is more thermally and chemically stable in solution than its unmodified counterpart ^[10].

After adopting HPG as the new anode binder, another preliminary study was performed on optimizing silicon dispersion in the infiltration solution. Utilizing dynamic light scattering (DLS) to measure particle size, it was determined that a one-hour sonication time was sufficient to disperse the SiNPs. Further sonication yielded the same amount of dispersion.

3. ANODE FABRICATION

3.1. Fabrication and Evaluation Equipment

- Centrifuge (capable of 5,000 G)
- NE-300 Just Infusion™ Syringe Pump plus 2mL syringes
- Sonicator
- Teflon mandrel (3.95 cm diameter)
- Teflon sheeting (0.005” thick)
- VMP Biologic 16-channel potentiostat

3.2. Coin Cell Components

Anode Components

- Alfa Aesar silicon nanoparticles ($\text{APS} \leq 50\text{nm}$, 98%)
- Refined Solvay Rhodia HPG (Jaguar HP 8 COS); see below for refinement procedure
- CNT Arrays (as produced by the Bradford Group; characteristics in Section 2.1)
- Timcal Super P Li carbon black
- De-ionized water (DI H_2O) and isopropyl alcohol (IPA)

Coin Cell Components

- MTI Corporation CR2032 coin cell components
- 0.4375” diameter copper foil current collector discs

- BASF Selectilyte™ LP-50 electrolyte; 1 M lithium hexafluorophosphate (LiPF_6) salt in 50:50 ethylene carbonate (EC)/ethylmethyl carbonate (EMC) solution
- Eagle Picher Fluoroethylene carbonate (FEC)
- 0.5" diameter lithium foil discs
- Extra LiPF_6 salt
- Celgard 2400 separator tape

3.3. Fabrication Procedures

There were three separate procedures for fabricating anodes: the solution mixing procedure, the anode infiltration and winding procedure, and finally coin cell fabrication procedure. There is a HPG refinement step preceding the fabrication process as documented below.

3.3.1. HPG Refinement

HPG was first refined before use in the infiltration solution to remove any high-molecular weight/insoluble material. To separate the undesirable material, centrifuge HPG solution, approx. 1% in water, at 5000 G for one hour. There will be a distinct visual difference between the desired HPG (clear) and undesired material (cloudy); separate the HPG, fully dry it and grind it into powder. Finally, HPG was premixed in DI water at a concentration of 10 mg mL^{-1} as a stock solution. HPG dissolution takes several hours so this step facilitates faster sample prep. This solution will be referred to as “premixed HPG”. Be sure to refrigerate premixed HPG and any kind of dissolved HPG to prolong shelf life.

3.3.2. Solution Mixing Procedure

1. Add the premixed HPG to the DI H₂O and IPA. Mix thoroughly by mechanical agitation for at least 10 minutes.
2. Mix in the SiNPs and sonicate the solution for one hour. A dispersion study indicated that sonication time more than one hour didn't yield better dispersion.

3.3.3. Anode Infiltration and Winding Procedure

Due to the highly process-driven nature of this thesis, the diagram of the infiltration setup is included in **Figure 2.4** as reference.

Figure 2.4: CNT felt infiltration equipment setup

1. Set syringe pump at desired infiltration rate (in mL min⁻¹) and the mandrel at the appropriate RPM. Infiltration parameters need to be calculated depending on the infiltration equipment available. The parameters used for this study are based on a 3.95 cm diameter mandrel and are listed in Table 2.1.

Table 2.1: CNT felt infiltration parameters

Anode Composition	No. of CNT Layers	Silicon Conc. (mg mL⁻¹)	Infiltration Rate (mL min⁻¹)	Mandrel RPM
55Si/35C	40	9.5	0.4	3.0
60Si/30C	62	15	0.4	3.0
50Si/40C	100	5.5	0.5	3.3

2. Cover mandrel with a layer of Teflon® sheeting and draw an initial layer of CNTs for winding as shown in **Figure 2.5**. Wind two layers onto the mandrel.

Figure 2.5: Drawing CNT felt for winding

3. Evenly coat the CNT felt on the mandrel with infiltration solution and then begin winding the CNT felt while the syringe pump deposits solution.
4. Using either the syringe pump or syringe markings, track the volume of infiltrated solution. Divide calculated infiltration volume by the number of CNT layers to determine the volume per layer rate. Because the infiltration equipment isn't exactly precise, monitor the infiltration volume per layer amount and adjust as needed.

Figure 2.6: Dried, infiltrated CNT felt

Figure 2.7: Cut CNT felt

5. After achieving the target solution volume and CNT layer count, leave the felt on the mandrel to dry while rotating for 4 hours or until infiltration solution no longer flows. When dry, slide the Teflon® sheet and CNT felt off mandrel, resulting in **Figure 2.6**; cut the CNT felt lengthwise for ease of handling as shown in **Figure 2.7**.

Figure 2.8: Cut CNT felt discs

6. Punch out anode felt to yield discs with 7/16" punch die as seen in **Figure 2.8**, weigh and dry before proceeding to coin cell fabrication.
7. (Optional) Consolidate the infiltrated CNT felt anode by pressing it onto a copper current collector at about 450 MPa or 65 ksi to thickness of about 13.5 μm (55/35), 11.5 μm (60/30) or 14.5 μm (50/40).

3.3.4. Coin Cell Fabrication Technique

Coin cells were fabricated per the layering scheme portrayed in **Figure 2.9**.

Figure 2.9: Coin cell diagram (adapted from [11]).

1. Place one stainless steel spacer into coin cell bottom and layer the anode-copper disc on top.
2. Deposit three drops ($\sim 150\ \mu\text{L}$) of electrolyte solution on top of the anode and layer a piece of separator on top. Ensure that the anode-copper disc does not shift from the center of the coin cell.
3. Deposit three more drops ($\sim 150\ \mu\text{L}$) of electrolyte solution onto the separator and layer on a piece of lithium foil, taking care to line it up with the anode.
4. Place a second stainless steel spacer on top of the lithium foil and place a spring on top of that.
5. Close the coin cell and crimp it. Allow cells to equilibrate overnight at open circuit voltage (OCV).

4. SAMPLE EVALUATION AND CHARACTERIZATION

4.1. Electrochemical Characterization

4.1.1. Galvanostatic Cycling with Potential Limitation

Galvanostatic cycling is a form of potentiometry used to analyze electrochemical cells.

Figure 2.10: A sample current waveform used in GCPL

A periodic current wave function as shown in **Figure 2.10** is applied to an electrochemical device and the resulting potential is measured. This thesis uses a modified potential window of 0.01 to 1.0 V to artificially limit the potential a working electrode experiences, hence the name galvanostatic cycling with potential limitation (GCPL). Cells can be cycled at calculated currents termed “C-rate” that indicate the time required to charge or discharge the cell. For example, a 1.0C rate results in a one-hour charge or discharge cycle while a 0.2C rate results in a five-hour charge or discharge cycle. C-rates are calculated via active material weight per anode as shown in Equation 2.1:

$$\frac{m_{Li} * F}{MW_{Li} * C \cdot rate} = \text{Charge/discharge current} \quad \text{Equation 2.1}$$

m_{Li} = mass of lithium in anode (g)

$C \cdot rate$ = charge/discharge time (s)

$F = 96487 \text{ C mol}^{-1}$ Faraday’s Constant

$MW_{Li} = 6.941 \text{ g mol}^{-1}$ Molecular weight of Li

4.1.1.1. Lifetime Cycle Testing

Samples were cycled 100 times with GCPL in a window from 10 mV to 1 V at a rate of 0.2C to illustrate cycling coulombic efficiency and any potential changes in cycling behavior.

4.1.1.2. Rate Capability Testing

As mentioned in Chapter 1, kinetic limitations can impact device performance at high redox reaction rates. For example, lithium diffusion rate in silicon might be the rate-limiting step in silicon-containing anodes; if subject to a high rate of charge and discharge, the silicon particles might not fully lithiate, reducing effective capacity. To test rate capability of the samples, they were cycled with GCPL at 0.2C, 0.5C, 1.0C, and 2.0C rates each for 10 cycles in a 10 mV to 1 V window.

4.1.2. Electrochemical Impedance Spectroscopy

While GCPL delivers information about device performance, Electrochemical Impedance Spectroscopy (EIS) can deliver information about device impedance. Impedance, Z , is the complex analog of resistance when a system is subject to alternating current. EIS utilizes a potentiostat to measure the current response of a steady-state device when it is subject to an oscillating potential over a user-selected range of frequencies. The corresponding current and phase change are measured to calculate the real and imaginary impedance components. Data can be represented either through a Nyquist plot, a comparison of imaginary and real impedance, or a Bode plot, a graph that relates impedance and phase angle to frequency.

Figure 2.11: Typical Nyquist plot for lithium ion cells [12].

Nyquist plots for LIBs are typically separated into five sections as shown in **Figure 2.11**.

Different effects can dominate in difference frequency regimes:

Section 1: In the high frequency regime, the EIS spectrum can show inductive behavior caused by metallic material in the cell.

Section 2: At the curve's intersection with the real impedance axis, the x-intercept indicates R_s , the series resistance of the system summed up together.

Section 3: The first feature is typically associated with the formation of SEI.

Section 4: The mid-frequency semi-circle represents charge transfer processes

Section 5: The tails present on lithium ion cell Nyquist plots indicate diffusion processes that dominate at low frequencies.

Figure 2.12: Typical equivalent circuit used to model silicon anode impedance [13].

Figure 2.13: Equivalent circuit from Guo et al. adapted to model samples in this study [13].

To analyze EIS data, users must model their systems to equivalent circuits. A typical equivalent circuit used to represent silicon-containing LIB anodes is shown in **Figure 2.12**. Constant phase elements (CPEs) are also known as non-ideal capacitors; CPEs include a capacitor in parallel with a resistor and a Warburg element in series. Each element of the equivalent circuit represents an electrochemical process, including ohmic resistances, SEI resistance, interphase electronic contact resistance and charge transfer resistance. This study will use a similar equivalent circuit as outlined in Figure 2.13 with a CPE replacing the last Warburg element, representing lithium diffusing into the SiNPs.

4.2. Physical Characterization

4.2.1. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a characterization method wherein a material's mass is measured as a function of increasing temperature (with constant heating rate) or as a function of time at elevated temperature in specified atmospheres (i.e., N_2 , air, argon, etc.). Results can provide information about phenomena such as decomposition mechanisms and second-order phase transitions.

In this study, a EXSTAR6000 TG/DTA 6200 was utilized to determine anode composition via thermal decomposition in air. The three anode components—CNTs, HPG and silicon—all decompose at different temperatures in air so it is possible to determine approximate mass composition of the anode sample. As shown blow in Figure 2.14, HPG decomposes around 250°C and CNTs decompose around 600°C. Due to the native oxide layer present, the SiNPs used in this study do not oxidize within the window of interest.

Figure 2.14: TGA of separate anode components

4.2.2. Scanning Electron Microscopy

A scanning electron microscope (SEM) rasters an electron beam across a material's surface. The electron-surface interactions can be recorded to reveal topographical and composition data about a sample. In this study, a FEI Verios 460L field-emission scanning electron microscope (FESEM) was employed to elucidate the anode structure and to determine silicon dispersion throughout the structure.

4.2.3. X-Ray Diffraction

X-Ray diffraction (XRD) was used to verify the composition of the as-received crystalline silicon nanoparticles. The measured XRD spectra should match that of silicon as shown in

Figure 2.15.

Figure 2.15: XRD spectrum for silicon nanoparticles showing representative peaks at $2\theta = 28.4^\circ$, 47.3° , 56.1° , 69.1° , and 76.4° at $\text{CuK}\alpha_1$ radiation [14].

5. DATA COLLECTION AND PROCESSING

5.1. Organization of Experiments

There were four primary sets of samples studied as detailed in **Table 2.2**. Group 1 and 2 are the primary experimental and control groups. Group 3 and 4 served as further experimental groups investigating the effect of silicon-CNT ratio on anode cycling performance. This study utilized three different solutions of differing silicon

concentrations for the three different CNT felts as outlined in **Table 2.2**. The infiltration solution compositions and corresponding sample groups are as outlined in **Table 2.3**.

Table 2.2: Four groups of samples studied in this thesis

Group #	Carbon Support	Silicon Content	Carbon Content	Binder Content
1	CNT	50%	40%	10%
2	Carbon Black	50%	40%	10%
3	CNT	40%	50%	10%
4	CNT	30%	60%	10%

Table 2.3: Composition of three infiltration solutions and their corresponding Group numbers from **Table 2.2** by weight percentages

Solution (Group)	Silicon Conc. (mg mL ⁻¹)	Silicon	Premixed HPG	DI H ₂ O	IPA
1 (1)	15	1.6%	32.7%	27.2%	38.5%
2 (2)	9.5	1.0%	20.8%	39.4%	38.7%
3 (4)	5.5	0.6%	12.1%	48.4%	38.9%

5.2. Data Processing

Lifetime cycling data was exported in EC-Lab software to a .txt format where Matlab was used to extract cycling times, dQ, charge/discharge capacity (mAh), and working electrode potential (V). The equivalent circuit as shown in Figure 2.13 **Error! Reference source not found.** was fit to each EIS curve to deconvolute the solution resistance (R_s), SEI resistance

(R_{SEI}), interphase electronic contact resistance, (R_{int}) and charge transfer resistance (R_{CT}).

Goodness of data was verified via Kramers-Kronig analysis.

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CHAPTER 3. RESULTS AND DISCUSSION

1. EFFECTS OF CONDUCTIVE SUPPORT ON CYCLING PERFORMANCE

As detailed in Chapter 1, the hypothesis of this study postulated that an infiltrated CNT felt structure would offer a more environmentally friendly lithium ion cell anode with improved cycling performance and rate capability compared to anodes fabricated with conventional carbon black conductive additives. This study was organized as shown in **Table 3.1**. Binder content was set at 10 wt% and conductive carbon additives filled the balance of materials.

Table 3.1: Coin cell characteristics

Si Content (wt %):	50%	55%	60%
CNT additive	X	X	X
CB additive	---	X	---

Table 3.2: Samples planned for study

Samples	Open Circuit Potential (V)	First Rev. Capacity (mAh g ⁻¹)
55/35 CNT	1.4 ± 0.4	2100 ± 410
55/35 CB	1.6 ± 0.8	2500 ± 820
60/40 CNT	1.0 ± 0.8	2050 ± 470
50/40 CNT	1.6 ± 0.9	910 ± 250

Going forward, samples will be referred to as “X/Y samples” where “X” denotes the silicon content and “Y” denotes the carbon content. Because the carbon additives were either the CNT felt or a standard carbon black powder, their respective samples will be termed “CNT samples” and “CB samples” henceforth. **Table 3.2** details the average open circuit voltages (OCVs) and initial reversible capacities for each group of samples.

1.1. Electrochemical Results: Cycling Performance of CNT vs CB Samples

This section will cover the samples comprised of 55/35 CNT and CB. Both groups of samples had approximately the same OCV and reversible capacity as seen in Table 3.2. However, the CB samples had a much larger standard deviation than the CNT samples. The samples in **Figure 3.1** through **Figure 3.3** are representative samples chosen for their similarity to group averages. Individual samples will be represented in later sections.

Figure 3.1: Discharge capacity of representative 55/35 CNT samples vs CB samples cycled at a 0.2C rate for 100 cycles

Figure 3.2: Coulombic efficiency (%) of 55/35 CNT samples vs CB samples overlaid on lifetime capacity data. Samples were cycled at a 0.2C rate for 100 cycles

Figure 3.3: Rate capability of 55/35 CNT samples and CB samples cycled at 0.2C, 0.5C, 1.0C, and 2.0C cycling rates for 10 cycles each

Table 3.3: Average capacity retention for 55/35 CNT and CB RC samples

Sample	0.2C	0.5C	1.0C	2.0C
55/35 CNT	---	62%	30%	6%
55/35 CB	---	59%	17%	2%

As seen in **Figure 3.1**, the CB samples had better initial reversible capacity than the CNT samples. However, the CB samples experienced more rapid specific capacity loss and they began underperforming CNT samples by around cycle 10. Both groups experience a slight bump in reversible capacity after the first cycle. By the end of lifetime evaluation, the CNT samples retained approximately 51% of their initial reversible capacity on average; the CB samples merely retained 26% on average. The CB samples also had a much more variable coulombic efficiency (CE%) when cycling as seen in **Figure 3.2**. **Figure 3.3** and **Table 3.3** compare the capacity retention of the CB and CNT samples in rate capability evaluation; the CB samples retained 58% capacity at 0.5C, approximately the same capacity as the CNT samples, as shown in, but performed worse at higher discharge rates, retaining 17% and 2% capacity compared to 31% and 6% retained by the CNT samples at the same respective discharge rates.

Because coulombic efficiency is a measure of charge storage efficiency, it is desirable for CE% to be both predictable and as close to 100% as possible. The CNT samples in **Figure 3.2** fulfill both metrics while the fluctuating CE% values of the CB samples do not. Both groups exhibit a characteristic low coulombic efficiency (~85%) on the first cycle caused mainly by irreversible Li consumption during initial SEI formation. The CE% values gradually increase to above 99% by cycle 55 for the CNT samples. The nature of the CB CE% values can indicate a physically changing microstructure where active material repeatedly disconnects and reconnects from the conductive network, respectively causing drops and spikes in CE%.

Figure 3.4: Silicon agglomerate pulverization during cyclic lithiation and de-lithiation [1].

The initial bump in specific capacity seen in **Figure 3.1** can most likely be explained by the exposure of additional fresh active surface area after the first cycle. This Si-CNT felt will inherently have SiNP agglomerates as a trade-off from solvent selection. Silicon volumetric expansion during lithiation can break up agglomerates as shown in **Figure 3.4**.

1.2. Electrochemical Results: Cycling Performance of CNT Samples (55/35 Si-CNT)

This section will present a broader view of the cycling behavior of the 55/35 CNT samples produced in this study. Several samples were selected to represent the entire data set of 55/35 CNT samples.

Figure 3.5: Representative discharge capacities of 55/35 CNT felt samples cycled at 0.2C rate for 100 cycles

Figure 3.6: Representative coulombic efficiency values of 55/35 CNT felt samples cycled at 0.2C rate for 100 cycles

Figure 3.7: Representative rate capability discharge capacities of 55/35 CNT felt samples cycled at 0.2C, 0.5C, 1.0C, and 2.0C cycling rates for 10 cycles each

Table 3.4: Capacity retention of 55/35 CNT felt rate capability samples

Sample	0.2C	0.5C	1.0C	2.0C
DH89-02 11RC	---	69.3%	44.2%	19.2%
DH89-02 12RC	---	61.5%	27.7%	2.3%
DH89-03 18RC	---	60.9%	29.0%	2.0%
Average	---	61.8%	30%	5.5%

Corroborating the specific capacity behavior seen in **Figure 3.1**, **Figure 3.5** displays a slight reversible capacity bump seen in the 55/35 CNT samples after the first cycle followed by a characteristic specific capacity decrease as SEI formation and lithium consumption occur throughout the lifetime of the cell. There is very little variation in coulombic efficiency values as seen in **Figure 3.6**. However as shown in **Figure 3.7** and **Table 3.4**, this homogeneity isn't as prevalent in the rate capability samples. Samples like DH89-02 11RC slightly skew the capacity retention data as seen in **Table 3.4**.

Figure 3.8: Representative differential capacitance curves for the first 10 cycles for the 55/35/10 infiltrated CNT felt samples (cycled at 0.5C rate for 100 cycles). Blue lines indicate the first cycle. As seen in the graph however, there is a discontinuity on the first cycle after the initial drop. This was due to a phenomenon seen in some samples that will be discussed in detail later in this section.

Differential capacitance (dQ/dV) curves as seen in **Figure 3.8** are used as an analogue to CV curves to determine reactions present during cycling as denoted by peak

location/potential. These peak locations and their corresponding reactions have been listed in **Table 3.5** ^[1].

Figure 3.9: Differential capacitance graphs for lithium ion cell anodes starting from the top: (1) First lithiation/de-lithiation cycle from <0.05-1.0 V; (2) Typical cycling behavior from ~0.1-1.0 V; (3) Typical cycling behavior from <0.05-1.0 V [2].

Starting at 1.0 V electrode potential and cycling down to 10 mV in **Figure 3.8**, it's possible to follow the blue line (indicating the first charge/discharge cycle) to find Peak I, *L*, as denoted in **Figure 3.9**. This peak signifies the transformation of crystalline silicon (cr-Si)

into amorphous $\text{Li}_{15}\text{Si}_4$ ($a\text{-Li}_{15}\text{Si}_4$) via **Reaction 3.1**. This reaction manifests on the differential capacity curve as a large initial peak at 90 mV ^[3]. Further cycling below 50 mV can result in a conversion of the $a\text{-Li}_{3.75}\text{Si}$ back into a crystalline phase ($\text{cr-Li}_{3.75}\text{Si}$) on a sufficiently long time scale (**Reaction 3.4**) ^[4]. It is important to note that the paper from which **Figure 3.9** is cited used a constant-current, constant-voltage cycling scheme that differed from the GCPL scheme used in this study. The that applies a low cycling current of 150 mA g^{-1} until a potential limit was reached, after which this potential was held implemented until 30 mA g^{-1} was achieved.

Table 3.5: Lithiation potentials and reactions adapted from Obrovac and Krause. L denotes a lithiation process while D denotes a de-lithiation process [2]

#	Figure 3.9 Label	Reaction Pot. (mV)	Reaction
3.1	I, L	90	$\text{cr-Si} + 3.75\text{Li} \rightarrow a\text{-Li}_{3.75}\text{Si}$
3.2	IV(a), $L1$	~300-250	$a\text{-Si} + 2\text{Li} \rightarrow a\text{-Li}_{2.0}\text{Si}$
3.3	IV(b), $L2$	~100	$a\text{-Li}_{2.0}\text{Si} + 1.75\text{Li} \rightarrow a\text{-Li}_{3.75}\text{Si}$
3.4	VI	~50	$a\text{-Li}_{3.75}\text{Si} \rightarrow \text{cr-Li}_{3.75}\text{Si}$
3.5	III, D	430	$a\text{-Li}_{3.75}\text{Si} \rightarrow 2.65\text{Li} + a\text{-Li}_{1.1}\text{Si}$
3.6	V(a), $D1$	~270-300	$a\text{-Li}_{3.75}\text{Si} \rightarrow a\text{-Li}_{2.0}\text{Si} + 1.75\text{Li}$
3.7	V(b), $D2$	~500	$a\text{-Li}_{2.0}\text{Si} \rightarrow a\text{-Si} + 2\text{Li}$
3.8	VII, D	430	$\text{cr-Li}_{3.75}\text{Si} \rightarrow a\text{-Li}_{1.1}\text{Si} + 2.65\text{Li}$

What is not seen in **Figure 3.9** is the discontinuous behavior seen in **Figure 3.8**. This anomaly stemmed from a slight rise in anode potential seen during the first lithiation cycle in several samples as shown in **Figure 3.10**. Because differential capacitance is calculated from dQ divided by dV , an increase in potential results in a positive dV , creating a discontinuity and a domain of positive dQ/dV values. This phenomenon isn't just limited to the sample listed in the caption. Approximately one-third to one-half of all coin cells exhibited this behavior and it tended to occur between 20 and 80 mV and the magnitude of this potential reversal was about 10 to 20 mV. As of the present, the cause behind this phenomenon is not yet known.

Figure 3.10: Anode potential increase as seen in sample DH89-03 Cell 27

Continuing past the first dQ/dV cycle, the characteristic peaks III, D in **Figure 3.9** corresponds to the conversion of $\text{cr-Li}_{3.75}\text{Si}$ to $\text{a-Li}_{1.1}\text{Si}$ as shown in **Table 3.5**, **Reaction 3.8**. However, this reaction does not appear in **Figure 3.8**; the first reverse sweep of the sample yields two de-lithiation peaks, denoted as characteristic peaks V(a) and V(b)

in **Figure 3.9**, corresponding to **Table 3.5**, **Reactions 3.6** and **3.7**. These two peaks V(a) and V(b) are associated with the two-step de-lithiation process of a-Li_{3.75}Si to a-Si and suggest that the lithium silicide present during de-lithiation is amorphous in nature. This is further corroborated by the fact that peak VII (**Table 3.5**, **Reaction 3.8**) is not present in any of the dQ/dV graphs.

It is possible that a a-Li_{3.75}Si → cr-Li_{3.75}Si conversion might exist in the 55/35 CNT samples due to the lithiation peak present at ~50 mV in subsequent cycles, represented by **Reaction 3.4** ^[4]. However, no such peak indicating the conversion of the crystalline lithium silicide back into an amorphous phase exists in **Figure 3.8**. It's possible that any crystalline-to-amorphous conversion peaks are being convoluted with peaks V(a) and V(b). It's also possible that the supposed amorphous-to-crystalline peak is an artifact of the cycling program, as it isn't as sharp as the characteristic peak in **Figure 3.9**. Since this study utilized a 0.2C cycling rate equating to ~720 mA g⁻¹, it is more likely that the amorphous-crystalline phase transformation has not had enough time to occur. Other studies investigating Si-CNT composite anodes have reported similar behavior ^[5,6]. Both Fu *et al.* and Yu *et al.* have reported similar dQ/dV plots without an amorphous-crystalline phase transformation peak, although they cycled their samples at 50 mA g⁻¹ and 100 mA g⁻¹ respectively. Continuing onto the subsequent lithiation curves in Cycles 2-10, the two major lithiation peaks present correspond to the reactions **Reaction 3.7** and **3.8**. As stated earlier, **Reaction 3.6** is possibly present during the lithiation process in addition to these two curves.

In summary, most of the differential capacitance behavior seen in this study has been documented in other anodes containing silicon and CNTs. The V(a) and V(b) peak shift to higher potentials seen between the first and succeeding cycles can be attributed to improved electrode reactivity after the first irreversible lithium formation reaction ^[6]. There is an unexplained region of potential increase during the first lithiation cycle occurring between 20 and 80 mV that creates a discontinuity in the dQ/dV graph. It is still possible to discern the location of the first peak.

Figure 3.11: Cross-sectional SEM image of 55/35 CNT felt sample

Figure 3.11 through **3.13** are SEM images taken of the 55/35 CNT felt samples. to ascertain felt structure and SiNP dispersion. Yildiz *et al.* have measured their nanotubes to be about 30 nm in diameter ^[7]. Through image analysis software, the CNTs in **Figure 3.13** were measured to be approximately 40 nm in diameter, indicating that the CNTs had very little

to no SEI layer. This is further confirmed by the bright appearance of the CNTs in **Figure 3.12**; since SEI is typically much less conductive than CNTs, it should appear as a darker region on SEM images.

Figure 3.12: SEM image of 55/35 CNT felt sample illustrating silicon dispersion characteristics

Figure 3.13: SEM image of individual CNTs in 55/35 CNT sample.

Further observing **Figure 3.11** and **Figure 3.12**, it can be noted that there seems to be large, dark regions of active material several hundred nm across interspersed with CNT bundles, indicating poor SiNP dispersion throughout the CNT felt. Again, non-ideal SiNP dispersion was deemed to be a trade-off for utilizing low-toxicity solvents.

1.3. Electrochemical Results: Cycling Performance of CB Samples (55/35 Si-CB)

The carbon black used in this study, TIMCAL Super P Li® has a gravimetric surface area of $62 \text{ m}^2 \text{ g}^{-1}$. This is comparable with the CNT felt utilized in this study which has a gravimetric surface area of $40 \text{ m}^2 \text{ g}^{-1}$ [8]. The two materials also have similar conductivities as discussed in Chapter 1. However, CB particles are considered 0D structures and must surpass a percolation threshold to offer conductive properties in a 3D structure. Comparatively, the layered CNT felt structure produced via winding has an inherent

through-plane conductive path due to the direct contact formed between CNTs as the felt winds.

Figure 3.14: Representative discharge capacities of 55/35 CB samples cycled at 0.2C rate for 100 cycles

Figure 3.15: Representative coulombic efficiency values of 55/35 CNT felt samples cycled at 0.2C rate for 100 cycles

Like the CNT samples, all CB samples exhibited an initial capacity increase during the first few cycles as seen in **Figure 3.14**; as theorized earlier in **Figure 3.4**, this phenomenon can probably be attributed to the exposure of fresh active surface caused by silicon's volumetric expansion and contraction during cycling. It is important to note that the capacity increase experienced by the CB samples lasts for several cycles and result in more capacity increase; on the other hand, the CNT samples only see one cycle of capacity increase at a much smaller degree. As discussed in Section 1.1 of this chapter, one possible cause for fluctuation in CE% and capacity reduction seen in **Figure 3.14** and **Figure 3.15** may be caused by cyclic electronic isolation of silicon active material in the anode as well as illustrated in **Figure 3.4**. This mechanism has been investigated by Ryu *et al.* who sought to control this phenomenon by studying silicon-carbon black anodes in pressurized lithium ion pouch cells. The pressurized pouches served to maintain ohmic contact between the silicon and carbon black throughout cycling ^[9]. Thus, they observed a ~50% improvement in specific capacity in pressurized samples as compared to the unpressurized samples.

Figure 3.16: Representative rate capability discharge capacities of 55/35 CB samples cycled at 0.2C, 0.5C, 1.0C, and 2.0C cycling rates for 10 cycles each

Table 3.6: Capacity retention of 55/35 CB felt rate capability samples

Sample	0.2C	0.5C	1.0C	2.0C
DH96-03 02RC	---	72.5%	40.0%	4.4%
DH96-03 09RC	---	68.4%	21.8%	2.2%
DH96-03 10RC	---	53.4%	5.6%	0.6%
DH96-03 12RC	---	56.2%	9.4%	1.0%
DH96-03 18RC	---	42.2%	8.8%	0.7%
Average	---	58.5%	17.1%	1.8%

As seen in **Figure 3.3** and further expanded upon in **Figure 3.16**, the CB rate capability samples could not retain capacity as well as the CNT rate capability samples at higher discharge rates. In **Table 3.6**, we see similar capacity retention at a 0.5C discharge rate by CB samples compared to the CNT samples in **Table 3.4**. However, the CB samples

experienced greater capacity loss at higher discharge rates with an average capacity retention of 17.1% at 1.0C and 1.8% at 2.0C. Also unlike the CNT samples, there isn't much capacity retention variation in the 2.0C regime.

Figure 3.17: Representative differential capacitance curves for the first 10 cycles for the 55/35 CB samples cycled at a C/5 rate. Blue lines indicate the first cycle.

The dQ/dV curves for the CB samples in **Figure 3.17** are nearly identical in nature to the dQ/dV curves for the 55/35 CNT samples in **Figure 3.8**. There's an initial lithiation peak at ~100 mV, indicating the lithiation of cr-Si into a-Li_xSi and subsequent delithiation peaks at 270 mV and 500 mV. The lithiation peaks at ~220 and 100 mV indicate the transformation of a-Si into a-Li_{2.0}Si and then a-Li_{3.75}Si. There's even a slight first cycle offset for the de-lithiation peaks at ~270 and ~500 mV, mirroring the 55/35 CNT sample behavior.

2. EFFECTS OF ELECTRODE COMPOSITION ON CYCLING PERFORMANCE

As discussed in **Table 3.2**, three groups of Si-CNT anodes were fabricated: 60/40, 55/35, and 50/40 CNT samples. This section will discuss the differences in cycling behavior and rate capability between the three different compositions.

2.1. Electrochemical Results: Cycling Performance of CNT Anodes

Silicon content was controlled during the felt infiltration process by using infiltration solutions of differing Si concentration.

Figure 3.18: Representative discharge capacities of CNT felt samples with varying Si content cycled at 0.2C rate for 100 cycles

Figure 3.19: Representative coulombic efficiency values of CNT felt samples with varying Si content overlaid on lifetime capacity data cycled at 0.2C rate for 100 cycles

Figure 3.20: Representative rate capability discharge capacities of CNT felt samples with varying Si content cycled at 0.2C, 0.5C, 1.0C, and 2.2C cycling rates for 10 cycles each

Table 3.7: Capacity retention of CNT-based samples with different silicon loading

Sample	Capacity Retention
60/30 CNT	70%
55/35 CNT	50%
50/40 CNT	40%

Table 3.8: Rate capability capacity retention of CNT-based samples with different silicon loading

Sample	0.2C	0.5C	1.0C	2.0C
60/30 CNT	---	65%	46%	12%
55/35 CNT	---	62%	30%	6%
50/40 CNT	---	54%	19%	3%

There isn't much of a rate capability difference between the 60/30 and 55/35 CNT felt samples as shown in **Figure 3.18**. Both exhibit approximately the same initial specific capacity and cycling behavior. The only minor difference between the two is the small capacity increase the 60/30 CNT samples in the first few cycles rather than an immediate decrease as seen in the 55/35 CNT samples.

2.2. Electrochemical Results: Cycling Performance of 60/30 CNT Samples

Below, **Figure 3.21** through **Figure 3.23** outline the cycling performance of the most heavily-loaded CNT felts studied in this project, the 60/30 Si-CNT felts.

Figure 3.21: Representative discharge capacities of 60/30 CNT felt samples cycled at 0.2C rate for 100 cycles

Figure 3.22: Representative coulombic efficiency values of 60/30 CNT felt samples overlaid on lifetime capacity data cycled at 0.2C rate for 100 cycles

Figure 3.23: Representative rate capability discharge capacities of 60/30 CNT felt samples cycled at 0.2C, 0.5C, 1.0C, and 2.0C cycling rates for 10 cycles each

Table 3.9: Capacity retention of 60/30 CNT felt rate capability samples

Sample	0.2C	0.5C	1.0C	2.0C
DH93-02 14RC	---	45%	44%	12%
DH93-02 16RC	---	72%	42%	13%
DH103-04 14RC	---	78%	52%	12%
Average	---	65%	46%	12%

Compared with the 55/35 CNT felt samples, the 60/30 CNT felt samples show a less drastic capacity drop in the first few cycles as seen in **Figure 3.21**; **Figure 3.22** shows that they also have consistent CE% values. However, the 60/30 CNT felt samples seem to have much better rate capability than the 55/35 CNT samples. The 60/30 CNT samples have much less capacity retention variation at 1.0C and 2.0C discharge rates. The dQ/dV curves in **Figure 3.24** share the same peak characteristics as prior dQ/dV curves and do not indicate any deviation in lithiation/de-lithiation behavior.

Figure 3.24: Representative differential capacitance curves for the first 10 cycles for the 60/30 infiltrated CNT felt samples (cycled at C/5 rate for 100 cycles). Blue lines indicate the first cycle.

Figure 3.25: Cross-sectional SEM image of 60/30 CNT felt sample

Figure 3.26: Cross-sectional SEM image of 60/30 CNT felt sample showing similar structure to 55/35 CNT felt sample

Figure 3.27: Cross section of 60/30 CNT felt sample. The highlighted areas indicate binder-rich regions.

The CNT felt cross sections in **Figure 3.25** through **Figure 3.27** reveal a structure like that of the 55/35 CNT felt samples. Similar to **Figure 3.12**, the bright CNTs in **Figure 3.26** do not have an SEI layer and again, there are distinct regions of excess silicon/SEI. What is different though, is that **Figure 3.27** reveals the presence of binder-rich regions in the anode. This is indicative of poor binder dispersion during synthesis.

2.3. Electrochemical Results: Cycling Performance of 50/40 CNT Samples

The last group of CNT felt samples displayed low capacities as compared to the other felt samples. **Figure 3.28** illustrates this with an initial capacity half that of the 60/40 and 55/35 CNT felt samples.

Figure 3.28: Representative discharge capacities of 50/40 CNT felt samples cycled at 0.2C rate for 100 cycles

Figure 3.29: Representative coulombic efficiency values of 50/40 CNT felt samples overlaid on lifetime capacity data cycled at 0.2C rate for 100 cycles

Figure 3.30: Representative rate capability discharge capacities of 50/40 CNT felt samples cycled at 0.2C, 0.5C, 1.0C, and 2.0C cycling rates for 10 cycles each

Table 3.10: Capacity retention of 50/40 CNT rate capability samples

Sample	0.2C	0.5C	1.0C	2.0C
DH89-01 02RC	---	29%	2%	0%
DH96-02 11RC	---	51%	16%	1%
DH103-02 06RC	---	83%	39%	6%
Average	---	54%	19%	3%

While analyzing the data, it becomes increasingly evident that while the lifetime cycling samples are very uniform, the rate capability samples have a very high variation. As mentioned earlier in this section, the 50/40 CNT samples had much lower capacity compared to their higher-loaded counterparts. It is possible that this low capacity stems from poor nanoparticle dispersion. Sample DH103 06RC in the rate capability study shown

in **Figure 3.30** has a low initial reversible capacity of $\sim 700 \text{ mAh g}^{-1}$ but jumps to greater than 2000 mAh g^{-1} in the following cycles at 0.2C and continues to exhibit capacities larger than the other two representative samples. The dQ/dV curves in **Figure 3.31** share the same peak characteristics as prior dQ/dV curves and do not indicate any deviation in lithiation/de-lithiation behavior.

Figure 3.31: Representative differential capacitance curves for the first 10 cycles for the 55/35/10 infiltrated CNT felt samples (cycled at C/5 rate for 100 cycles). Blue lines indicate the first cycle.

Figure 3.32: Cross-sectional SEM image of 50/40 CNT felt sample illustrating ideal dispersion

Figure 3.33: Cross-sectional SEM image of 50/40 CNT felt sample illustrating poor dispersion

While some regions such as **Figure 3.32** had adequate silicon dispersion, more common areas such as **Figure 3.33** further illustrate the poor silicon dispersion in the infiltrated CNT felts.

3. PHYSICAL CHARACTERIZATION

3.1. Thermogravimetric Analysis

It is possible to ascertain Si-CNT anode composition via thermogravimetric analysis (TGA) in air. Samples were taken from the infiltrated CNT felt and dried CB slurry. They were then placed in alumina crucibles and heated from room temperature to 800°C in air at a rate of 10°C min⁻¹. As shown in **Figure 3.34**, HP guar and CNTs both degrade before SiNPs in air; HP guar degrades around 300°C and the CNTs degrade after 600°C. Silicon normally oxidizes around 800°C in air but the SiNPs don't significantly oxidize due in part to the native oxide layer and in part to the short time scale of the TGA; longer holds at 800°C would be required to oxidize the silicon core in the SiNPs. Based on their respective degradation temperatures, CNT felt composition was calculated based on the remaining weight percentage.

Figure 3.34: TGA in air of CNT felt components

Figure 3.35: TGA of 55/35 CNT felt samples confirming composition of approx. 55wt% silicon, 35wt% CNTs, and 10wt% binder

Figure 3.36: TGA of 55/35 carbon black slurry confirming composition of approx. 55wt% silicon, 36wt% carbon black, and 8wt% binder

Figure 3.37: TGA of 60/30 CNT felt samples confirming composition of approximately 60wt% silicon, 30% CNT, and 10wt% binder

Figure 3.38: TGA of 50/40 CNT felt confirming composition of approximately 50wt% silicon, 40wt% CNTs, and 10wt% binder

Table 3.11: Summary of proposed sample composition and measured sample composition (via TGA)

Group #	Proposed (wt%)			Measured (wt%)		
	Si	C	HPG	Si	C	HPG
1 (CNT)	55	35	10	57	32	11
2 (CB)	55	35	10	55	36	8
3 (CNT)	60	30	10	60	30	10
4 (CNT)	40	50	10	50	40	10

Figure 3.35 through **Figure 3.38** confirm the composition of the infiltrated CNT felt anodes used in this study. There was slight variation among samples within sample groups but the difference was no more than a few percentage points.

3.2. XRD Characterization

Figure 3.39: Measured XRD spectra of silicon nanoparticles as received from Alfa Aesar

Literature states that crystalline silicon yields peaks at $2\theta = 28.4^\circ, 47.3^\circ, 56.1^\circ, 69.13^\circ$, and 76.4° when analyzed with $\text{CuK}\alpha$ radiation^[10]. The XRD spectra measured peaks at $28.4^\circ, 47.3^\circ, 56.0^\circ, 69.1^\circ$, and 76.4° , confirming both the composition and crystallinity of the silicon used in this study.

4. DISCUSSION

There was a high degree of variability among coin cell sample performance in this study as illustrated by the open-circuit potentials of the coin cells as shown earlier in Error! Reference source not found.. This variability is due largely in part to the highly process-driven aspect of this project; achieving sample uniformity was challenging due to the factors such as binder solubility, achieving adequate SiNP dispersion, as well as CNT array quality. Much of the sample-to-sample variation seen in this study can be attributed to inadequate silicon and binder dispersion.

Figure 3.40: TEM image of silicon nanoparticle agglomerate from 55/35 CNT felt infiltration solution

A preliminary study measured particle dispersion via dynamic light scattering (DLS) which revealed that a one-hour sonication in an aqueous IPA solution yielded ~500 nm agglomerates, represented by a TEM image of an observed SiNP cluster in **Figure 3.40**. The cluster size was deemed acceptable and the project continued.

Figure 3.41: Anomalous cycling behavior from study (Sample DH93-01 Cell 08)

However, the post-mortem SEM imaging in this chapter confirms an abundance of silicon-rich areas and possibly binder-rich areas. Because this study focused on using low environmental impact solvents, a less-than-ideal particle dispersion was accepted as a suitable trade-off for a more elementary fabrication process. As such, the intended anode structure was to have silicon nanoparticle clusters well-dispersed among the CNT felt to accommodate silicon's volumetric expansion while maintaining good ohmic contact. These agglomerations could feasibly be responsible for anomalous cycling behavior seen in some samples of the study such as behavior shown in **Figure 3.41**.

Figure 3.42: Krause et al. data mirroring failure seen in Si-CNT samples [11.]

The data depicted in **Figure 3.41** came from a 55/35 CNT sample that was discarded as a failed sample; this phenomenon was observed in other samples in this study as well. Krause, A. *et al.* reported a similar phenomenon in their lithium-sulfur full-cell samples as seen in **Figure 3.42**; they termed the phenomenon simply as “cell instability” and alluded to lithium dendrite formation caused by high charge and discharge currents as its cause. Krause *et al.* used a 0.2C rate to charge and discharge their samples. Therefore, higher silicon loadings result in higher charge and discharge currents. It can be seen in **Figure 3.42** that higher silicon loading results in earlier cell instability.

Figure 3.43: Uneven felt drawing resulting in “cavities” in CNT array

Another source of sample dissimilarity stemmed from a degree of variation among the as-received CNT arrays manifesting as abnormal winding behavior.

Figure 3.44: CNT gaps caused by cavity formation

Figure 3.45: CNT "finger" formation during winding

The felt would sometimes wind in a non-uniform manner, resulting in “cavities” as highlighted in **Figure 3.43**. In addition, some CNT regions would cease winding altogether to form CNT “fingers” as seen in **Figure 3.45**. It’s possible that the behavior in **Figure 3.43** is the result of non-uniform CNT length. A region of shorter CNTs should wind at a faster rate to match the wind rate of the longer CNTs. As a result, cavities like the one seen

in **Figure 3.43** can form. As the CNT sheet winds, individual CNT strands can entangle with the sides of these cavities, growing the cavities laterally; if left unchecked, these cavities would create gaps in the CNT sheet as shown in **Figure 3.44**. If a cavity or fingers formed during infiltration, the entire winding process had to be stopped to remove the offending segment to ensure felt uniformity. Thus, some infiltrated CNT felts had local structural inconsistency due to the break in infiltration process.

Figure 3.46: Cell instability relating to amount of FEC present [12].

One other major factor that can play into sample non-homogeneity is the formation of a crystalline lithium-silicide phase below 70 mV vs Li/Li^+ . The $\text{cr-Li}_{3.75}\text{Si}$ phase has been documented as a hindrance in silicon anode performance ^[4]; its formation from $\text{a-Li}_{3.75}\text{Si}$ is associated with a large overpotential which reduces operating potential. Therefore, selecting the lower potential bound of a cycling window becomes nontrivial. This study cycled to 10 mV, well below the 70 mV threshold and as such, $\text{cr-Li}_{3.75}\text{Si}$ formation would be of concern for future studies.

Samples in this study did not experience significant capacity drop due to excessive SEI formation due in part to the implementation of FEC. Per Jung, R. *et al.*, FEC is preferentially reduced in lieu of other solvents over the lifetime of a device and it should be included as a major constituent of electrolyte solvents upwards of 10wt%. **Figure 3.46** provides an example that compares four samples of differing FEC content. Samples containing less than 10wt% FEC all fail within 300 charge/discharge cycles. The findings made by Jung, R. *et al.* have been independently confirmed by Petibon *et al.* ^[13].

5. REFERENCES

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CHAPTER 4. CONCLUSION

This study achieved two primary objectives. First, the hypothesis was confirmed; infiltrated CNT felt anodes did indeed perform better than anodes containing CB as a conductive additive. Although the CB samples had a higher initial capacity, they experienced a much faster capacity fade as compared to the CNT samples. Furthermore, the CE% behavior was much more consistent in the CNT samples as compared to the CB samples. As confirmed through TGA, three sets of infiltrated CNT felt anodes of 60/30, 55/35, and 50/40 Si/CNT content were produced as well as one set of CB slurry anodes matching the 55/35 CNT sample composition. The samples were characterized electrochemically with GCPL and EIS to ascertain their lifetime cycling performance, rate capability, and the electrochemical processes present during anode operation.

The second objective of this thesis was to develop a novel fabrication method for a silicon-containing anode for use in LIBs with the CNT array produced by the Bradford Group. Similar work has been done in the past such as spray-infiltrating the CNT felt with polymer binders or electrospinning carbon nanofibers containing SiNPs; however, this study sought to marry several of these concepts into a fabrication technique that produced effective silicon-containing anodes of matching performance with similar Si-CNT composite anodes. While most silicon-containing anodes today utilize expensive techniques or harsh chemicals during fabrication to mitigate inherent materials limitations, this study sought to approach the objective from a different perspective. The primary stipulation for this objective was to eschew stronger, more dangerous solvents in favor of low-environmentally impacting solvents and chemicals. The resulting fabrication process

evolved into an in-situ liquid infiltration of CNT felt with a solution containing the silicon active material and the HPG binder; the felts were infiltrated with and wound to calculated values. After drying, the CNT felts were cut into anode discs which were then consolidated via a hand press onto a copper current collector. The anode-copper discs were then incorporated into standard coin cells to assess anode performance. The coin cells used a modified BASF electrolyte solution of 1 M LiPF_6 dissolved in a mixture of EC, EMC and FEC. Lithium foil was used as the counter and reference electrodes in a standard two-electrode half-cell configuration.

1. EFFECT OF CONDUCTIVE ADDITIVE ON CYCLING PERFORMANCE

As confirmed through TGA, a set of infiltrated CNT felt anodes and a set of CB slurry anodes were produced with 55/35 Si-C content. As stated earlier, the CNT felt anodes had better cycling properties than the CB slurry anodes. Although the CB samples had better initial capacity, they experienced a much faster capacity fade and much more variable CE% behavior; the capacity fade and CE% behavior seen in the CB samples were attributed to the inability of carbon black in maintaining good ohmic contact with the SiNPs. The intermittent issue of maintaining good ohmic contact was exacerbated by the cyclic swelling and shrinking of the silicon nanoparticles.

The corresponding dQ/dV curves for the 55/35 CNT and CB samples revealed anomalous behavior during the first lithiation cycle as some samples experienced an anode potential increase in low voltage regimes. There was no clear correlation between this behavior and sample composition; both CNT and CB coin cells exhibited this behavior as well as

samples from each composition. The cause was still undetermined at the time of this thesis. Subsequent cycling of the 55/35 CNT and CB samples revealed standard lithiation and de-lithiation behavior so the phenomenon was confined to the first cycle only.

Through analysis of the SEM images, it was determined that the silicon dispersion was not nearly adequate. An ancillary silicon dispersion study was done on the infiltration solutions used and it was determined that a solution containing 55% DI H₂O, 45% isopropyl alcohol was sufficient to disperse the SiNPs with aggregates less than 500 nm in diameter per dynamic light scattering (DLS) measurements. Having this non-ideal particle dispersion was deemed to be an acceptable trade-off for using low-toxicity, aqueous solvents. The intended anode structure was to have silicon agglomerates well-dispersed among a CNT forest but the micron-sized aggregates were present in the observed felt structure. As such, it's understandable why the anodes experienced constant degradation across their lifetime.

2. EFFECT OF ANODE COMPOSITION ON CYCLING PERFORMANCE

As confirmed through TGA, two sets of infiltrated CNT felt anodes measuring 60/40 and 50/40 Si/C content were produced. The cycling performance of these two compositions was compared to that of the 55/35 CNT felt samples. While there was no appreciable difference in cycling performance between the 55/35 and 60/40 CNT samples, there was a marked decrease in specific capacity between the 55/35 and the 50/40 CNT samples however. Through SEM imaging, the dispersion was seen to be very like the 55/35 and 60/40 samples. The corresponding dQ/dV curves for the 60/40 and 50/40 samples revealed the same lithiation and de-lithiation behavior as the 55/35 samples. Anomalous behavior

was again observed during the first cycle as some samples experienced an anode potential increase in low voltage regimes during the first lithiation process.

CHAPTER 5. FUTURE WORK

First and foremost, more work needs to be done to better understand this system and explain unresolved phenomena. As shown and discussed in Chapter 3, a significant number of samples exhibited an unexplained potential increase in low potential regimes below 100 mV. This phenomenon hasn't been observed in literature yet and further study needs to be done to elucidate why and how it occurs. Reproducing this phenomenon would be the first step to determine whether it's an actual materials-based property or simply an artifact of the analysis method used. Furthermore, there was wide variability in the coin cells produced for this study as evidenced by the standard deviation in cell capacity. Much of it can probably be tied to anode fabrication. Reducing this variability is key to producing more consistent samples. Controlling silicon-to-binder ratio would be the first step; another possible step would be to reduce the silicon content of the anode in order to minimize silicon agglomeration. In addition, more care needs to be taken when selecting analysis parameters in future studies. Due to the novelty of this study, a very general set of analysis methods were used to capture coin cell data. Narrowing experimental variables such as cycling potential window is crucial in eliminating undesirable phase transformations and lithiation processes. Taking these measures is one possible step towards de-convoluting the anomalous data as discussed in Chapter 3.

Also, more data needs to be collected for EIS analysis to investigate materials properties. Moreover, many researchers collect EIS data at regular intervals while cycling their samples; this allows them to analyze coin cell property evolution during cycling. This study

simply collected EIS data at the end of lifetime cycling which doesn't give any insight into early phenomenon such as SEI formation and lifetime processes such as FEC consumption. Because much of this project's motivation was based on developing a new low-cost method of fabricating a silicon-containing anode, scalability is also an avenue for future study. It's possible to fabricate larger and different CNT arrays than the one used in this study. The Bradford group can tailor the length and diameter- and consequently number of walls- of the CNTs as grown in their arrays. Investigating how CNT length and diameter influence anode cycling is one possible study. Also, guar gum has only just entered the conversation as a potential silicon anode binder; HPG has been investigated even less. It isn't as well established or investigated as traditional binders like PVDF or CMC. HPG may very well have wider application in LIBs; in fact, preliminary work has been done on HPG/SiO₂ composites as LIB separators ^[1], not much has been done otherwise. Further study may be done on HPG/electrolyte interaction as well as its ionic conductivity when solvated.

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