A SYSTEMATIC STUDY OF STABILIZATION METHODS FOR
MECHANICALLY MILLED SILICON-CARBON
NANOCOMPOSITE ANODE MATERIALS

A Thesis in
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by
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Abstract

With a theoretical specific capacity of more than 4000 mAh/g, an order of magnitude improvement over the capacity of graphitic carbon, silicon has been examined as an improved anode material for lithium ion batteries. In this thesis, the performance of a silicon-carbon nanocomposite material produced via a simple mechanical milling process is examined and optimized through the systematic exploration of several important parameters. Commercially available silicon nanoparticles in a 1:1 ratio to conductive carbon are used to achieve a gravimetric energy density of almost 1000 mAh/g after 150 cycles following a study of silicon-carbon ratios, binder materials, electrolyte composition, and silicon nanoparticle size. Additionally, the effect of the electrolyte additive fluoroethylene carbonate on the silicon anode during cycling was studied utilizing high resolution SEM imagery of post cycling electrodes and the mechanical destruction of the silicon anode cycled without the FEC additive in the electrolyte is clearly contrasted with the nearly pristine structure of an electrode cycled in electrolyte containing 10% FEC.
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Dedication

For my wonderful wife, Amy. You are and always will be the center of my life.
~ To Love and Cherish ~
Chapter 1

Introduction

1.1 Background

Along with the significant number of battery powered consumer electronic devices utilizing rechargeable lithium ion batteries, there are two large scale applications calling for new and improved battery technologies. With efforts to increase the role of renewable energy sources including solar and wind energy there is a corresponding need for energy storage on the grid-scale in order to effectively utilize the energy that these produce. The energy produced from these sources is not constant nor is it always produced during times of peak energy use. This application demands batteries that are highly stable over a long cycle life with sufficient energy density to allow for practical implementation.

In the United States, the Batteries for Advanced Transportation Technologies (BATT) Program is the Department of Energy’s research program that is seeking to develop high performance batteries for electric vehicles and hybrid electric vehicles (EV’s and HEV’s). EV’s and HEV’s require energy storage solutions that have the capability to support improved vehicle range and performance as well as long term reliability by offering increases in energy density, peak power output, and long term coulombic efficiency. Additionally, within this program the DOE has identified six basic research tasks: anodes, cathodes, electrolytes, cell analysis, diagnostics, and modeling. The first three of these fields form the fundamental building blocks of any battery and there are a multitude of researchers working within each of these fields just under the BATT program’s funding and direction.
and while this is a significant program within the lithium ion battery material research community it is by no means the only large research program related to lithium ion battery research. With all of this motivation behind the efforts to develop improved battery materials, there have been significant steps to improve cathode materials which we will discuss in more detail in Chapter 2.

In conjunction with the cathode material research there have also been important steps taken to improve anode materials. The most important development of this research has been the switch from graphite based materials to materials utilizing chemical elements that have much higher theoretical capacity. The use of new elements means that research is faced with a new set of challenges in order to make effective use of these same elements. This process will have to be completed before a new material can take the place of graphite as the commercial standard.

1.2 Overview of Lithium Ion Batteries

Lithium ion batteries can make use of a variety of cathode and anode materials but are all governed by similar processes. The basic configuration of a lithium ion battery can be visualized as a “sandwich” with the cathode material is coated onto a current collector (typically a thin piece of tin foil on the cathode side of the battery) and the cathode material is separated from the anode material (coated onto a copper current collector) by a thin separator membrane that prevents direct electron transfer but allows lithium ions in the electrolyte to pass through and thus complete the circuit. In our research we use coin cell type batteries configured as shown in an expanded view in Figure 1.1.

The charge discharge cycle relies on the ability of the cathode material to accommodate lithium atoms in the interstices in its crystal structure, and in a graphitic anode the lithium atoms can also be stored in the interstices between the layers of carbon. The higher affinity of the cathode material for the lithium ions produced by an oxidation half-reaction means that work can be done by the electron flow through the connected circuit. The electrons are prevented from directly exchanging between the anode and the cathode with a porous separator that allows lithium ions to pass through in a liquid electrolyte such as the lithium salt LiPF$_6$ dissolved in organic solvents.
Figure 1.1: Expanded view diagram of coin cell type lithium ion battery.

For a lithium ion battery comprised of a graphitic carbon (C$_6$) anode and the relatively common spinel structured lithium-cobalt-oxide (LiCoO$_2$) cathode, we can describe oxidation-reduction reactions corresponding to the discharge of the battery as follows:

\[
LiC_6 \rightarrow C_6 + Li^+ + e^- \quad (1.1)
\]

\[
CoO_2 + Li^+ + e^- \rightarrow LiCoO_2 \quad (1.2)
\]

The charging reactions are obviously the reverse of Eqs. (1.1) and (1.2) and require an applied voltage to overcome the energy barrier. In

### 1.3 Cathode Materials

There are several cathode materials for lithium ion batteries that are currently in widespread use. These materials fit into several structural categories and are often described using their crystallographic structure. However, for the purposes of this study the cathode material is unimportant as our test cells are assembled as half cells with the anode paired with lithium foil instead of a cathode.
1.4 Anode Materials

The graphitic carbon electrode utilizes the interstices between the layers of carbon to store the lithium ions while the high electrical conductivity of carbon allows for effective electron transfer through the anode material. Because of the layered structure of the graphite and the small size of lithium ions, graphitic carbon also has the desirable characteristic of undergoing very little volumetric expansion during the lithiation process. Unfortunately, graphitic carbon also has a limit to its theoretical capacity that is becoming a limiting factor to improving the gravimetric energy density of lithium ion batteries. With a theoretical gravimetric energy density of 372 mAh/g, the capacity of carbon is being outstripped by newer cathode materials and with other materials that offer much higher theoretical capacities. Some of the most promising materials are ones that alloy with lithium rather than relying on intercalation to transport lithium ions to interstitial sites. Two of the most promising of these materials are tin and silicon which have theoretical capacities of 994 mAh/g for Li$_{22}$Sn$_5$ and 4200 mAh/g for Li$_{22}$Si$_5$ respectively. [7, 13]

1.4.1 Silicon as an Anode Material

The ten-fold capacity increase that silicon offers is not without significant challenges. Si undergoes a large volume change during Li-alloying and dealloying. For silicon, there is a 270–300% volume expansion during the Li-alloying process.[3, 13] While these volume expansions are reversed in the dealloying process, they still can still cause fracturing and cracking in both the Si particles themselves as well as in the electrode. This can effectively pulverize the electrode within a few charge-discharge cycles resulting in the loss of contact with regions of the electrode and a correspondingly drastic drop in the electrode capacity. This results in the typically exponential capacity decay exhibited by silicon electrodes.

The current silicon anode research is focused on ways to mitigate the capacity loss during cycling. There are also practical considerations having to do with use of Si as an anode material in commercial applications. Chiefly, cost and time of synthesis and/or manufacture of the materials. With many of the relatively successful silicon based materials utilizing expensive or difficult to produce materials such as graphene or processes including the growth of nanowires.
1.5 Thesis Outline

The subsequent chapters are organized into the following topics:

Chapter 2 is a review of literature detailing the benefits and problems with silicon anode materials as well as the current efforts to improve the performance of silicon and silicon based anodes. The current research falls primarily into three areas: various silicon-carbon structures; novel binders and electrode preparation; and work to improve the solid electrolyte interface (SEI) including electrolyte additives and coating techniques.

Chapter 3 details the methodology used in this work to produce materials and electrodes as well as to characterize the materials and test the electrode performance.

Chapter 4 presents the electrochemical performance data from our research. We provide the results of tests related to the Si:C ratio, binder type and content, and silicon nanoparticle size.

Chapter 5 includes a look at the mechanical decay of electrodes as a function of electrolyte contents. Electrodes containing NaCMC as the binder material were examined using SEM imaging in their pristine state and then after one cycle and after ten cycles using electrolytes containing no additives, 10% VC additive, and 10% FEC additive. SEM images are shown with the corresponding electrochemical cycling data to show the decay of the electrode structure during cycling.

Chapter 6 contains a concluding statement and some possible future research to be explored.
Chapter 2

Literature Review of Previous Research

The progress of lithium ion battery technology research has been largely cathode material driven, however there has also been a significant amount of research on new anode materials including alternative carbon based structures and alloying materials including germanium, tin, and silicon. Silicon has been recognized for 25 years as a material with very appealing possibilities as a replacement for the current (standard) graphitic anode materials for use in Li-ion batteries. All of these materials offer improved performance; germanium and tin have theoretical capacities of 1623 mAh/g and 994 mAh/g respectively both of which are more than three-fold increases over the capacity of a graphitic carbon anode. However, with a theoretical capacity over 4000 mAh/g (4008 mAh/g for Li$_{21}$Si$_5$) (Corresponding to Li$_{15}$Si$_4$) and its abundance as an element, silicon is the most promising of these elements and a great deal of research has been done to harness silicon for lithium ion battery use. [2, 4, 5, 9]

2.1 Silicon as an Anode Material

Silicon (and other alloying anode materials) store lithium by alloying with it in contrast to the intercalation process used for lithium storage in graphitic structures, wherein Li$^+$ ions are inserted between the layers in the graphite structure during lithiation and extracted during delithiation, which correspond to the dis-
charge and charge cycles respectively in a full battery cell. [5] During the alloying process the reaction $x\text{Li}^+ + \text{Si} + xe^- \rightarrow \text{Li}_x\text{Si}$ occurs which results in a large volume increase (310\% for \text{Li}_{22}\text{Si}_5 and 270\% for \text{Li}_{15}\text{Si}_4). [3, 10] This change in volume also requires significant structural changes within the material as the bonds between silicon atoms must be broken apart and reformed with lithium atoms. In crystalline silicon, this process is even more sharply pronounced as there is a two phase lithiation process with a sharp (nanometer scale) reaction front where the crystalline silicon’s bonds are broken apart. The lithiation process itself has been studied and it has been found that the amorphous and highly lithiated silicon that forms at the reaction front is \text{Li}_x\text{Si} with $x = 3.4 \pm 0.2$.

This makes the utilization of silicon much more difficult than typical electrode materials; a graphitic carbon based electrode material only experiences a relatively small change in volume ($\sim 12\%$) which plays a role in maintaining the stability of the electrode during cycling. [3] With the $\sim 300\%$ volume increase, crystalline silicon has typically shown significant irreversible capacity loss as an electrode material. The energy required to break apart the crystalline structure is not recovered fully after the first lithiation cycle. Additionally, crystalline silicon shows much more tendency to fracture and break apart due to the increased stresses involved in the initial phase of lithiation in which the crystalline form is transformed into amorphous and highly lithiated silicon at the reaction front. [9]

It is the combination of the irreversible capacity loss during the first cycle and the general capacity fade during cycling of silicon anodes that have hampered the practical application of silicon as an anode material for lithium ion batteries. In this chapter, we will review some of the notable research efforts to overcome the capacity loss due to volumetric expansion and contraction as well as irreversible capacity loss in order to utilize the highly promising theoretical capacity of silicon.

One of the most basic improvements that has been implemented in many studies of silicon anodes to decrease first-cycle irreversible capacity loss is the use of amorphous silicon as the starting material rather than crystalline silicon structures. From there the research into (amorphous) silicon as an anode material has progressed down several avenues. One of the most important things to understand in all of these is the nature of the alloying/de-alloying process and the role that it plays in the performance of the electrode over time.
Some of the early research proving that silicon has promise as a lithium ion battery anode and later research into the performance of silicon with respect to electrolytes has been done utilizing silicon thin film electrodes. In some of the early research into silicon as an anode material, Bourderau et al. among others showed that a silicon thin film electrode could produce high capacities, but showed the exponential decay of capacity, particularly when the thickness of the silicon is greater than approximately 100 nm. [5]

![Figure 2.1: Statistics showing the critical size \( D_c \) around 150 nm. In the non-fracture zone \( D < D_c \), the SiNPs did not crack or fracture upon first lithiation (open stars). When \( D \) was larger than \( D_c \), the SiNPs always cracked and fractured (solid stars). With decreasing \( D \), the ratio of \( t/D \) (\( t \), the Li xSi shell thickness when first crack appeared) monotonically increases from about 0.2 to 0.6 (red dots), indicating a relatively delayed crack event in smaller SiNPs, consistent with the final entrance into the nonfracture zone. *Figure and caption from* [34].

This interesting note about the thickness of the electrodes used and the tendency of the electrodes to fracture upon cycling is paralleled by several other studies having to do the relation between the size of silicon particles and the tendency to
self fracturing during cycling. [11, 34] Liu et al. found that there is a threshold diameter below which silicon particles do not display the tendency to fracture themselves during cycling by using in situ TEM to study silicon nanoparticles of different sizes during lithiation. This was able to show the process of the lithiation and verify that below the threshold diameter of $\sim 150$ nm silicon nanoparticles (SiNPs) are able to cycle without fracturing. Figure 2.1 illustrates the results of their work and shows the data behind the determination of the critical particle diameter ($D_c$). [34]

### 2.2 Silicon-Carbon Structures

There have been many studies of ways to create a silicon-carbon material that uses the stability and electrical conductivity of carbon in its various forms in order to improve the electrochemical and mechanical performance of amorphous silicon.

Some of these materials fall into a category that could be described as carbon contained silicon and the more successful of these materials have been engineered to contain buffer space to allow for the expansion of the silicon that is contained within either a carbon framework or shell.

Starting in around 2011, several groups began reporting materials utilizing a carbon capsule or shell to contain the silicon nanoparticle(s). J. Bae first reported a process for producing carbon microcapsules with diameters ranging from 2.5 µm to 30 µm containing multiple silicon nanoparticles (average diameter of 100 nm) utilizing a polymer process. as shown in Fig. 2.2. These microcapsules were shown to contain some buffering space, although no relationship between buffer space and the volume of the contained silicon was provided or postulated. These microcapsules were able to produce first cycle discharge capacities over 1300 mAh/g at 0.2 C rate between 1.5 and 0 V with a coulombic efficiency of 78 % and after 30 cycles the capacity retained was as high as 60 %. [22]

Several groups have continued with the carbon shell concept using both capsules containing multiple silicon nanoparticles and using carefully controlled buffer space. [21, 26, 29, 30] Efforts to produce shells around each individual silicon nanoparticle have been particularly interesting and work by Chen et al. and Iwamura et al. have shown that there is an optimal buffer size of approximately 3
times larger than the volume of the silicon. Above this ratio it seems that the silicon may become disconnected from the carbon shell or perhaps the shell is just too fragile to maintain structural integrity. Figure 2.3 shows TEM images of the materials produced by Chen et al. using SiO$_2$ coating over the silicon nanoparticles to create a buffer that is then etched away after using TEOS to create a carbon coating over the SiO$_2$.

These materials offer significant advantages including the compatibility with traditional slurry coating techniques, which gives them an advantage over some silicon carbon composites that have been produced utilizing carbon nanotubes or nanowire based materials. However, the process to fabricate these materials is still a multi-stage process that requires carefully controlled parameters to achieve optimal materials.
2.3 Effect of Binders

There has been significant research into new binders for Si-anodes and into the exact methods of binder-silicon interaction. Polyvinylidenedifluoride (PVDF) binders have been shown to unable to effectively maintain the structural integrity (and thus the electrochemical performance) of silicon based electrodes. The weak van der Waals forces that attach PVDF to silicon and possibly the softness of PVDF when immersed in electrolyte solvents result in a distinct loss of cycling performance when compared to other binders in anodes containing silicon. [13, 14, 15, 16, 17]
There are very distinct differences in performance depending on the binder used and also several important criteria for dealing with the problems inherent in the expansion of silicon. All of the successful binders for silicon have been stiffer than the typical PVDF binder and ideally they should have little to no interaction with the electrolyte solvents while maintaining a strong bond to the silicon to withstand the forces that arise due to the expansion and contraction of the silicon during cycling. Interestingly, sodium-carboxymethylcellulose (NaCMC) has been tested as a replacement and shows increased performance. NaCMC provides stable performance when used with graphite and its stiffer, brittle nature produces much more stable electrochemical cycling performance. Additionally, Hochgatterer et al. has shown that the degree of substitution of terminal carboxylic acid sites has an effect on performance. A covalent bond is formed by a condensation reaction between carboxylic acid sites on the NaCMC and the native hydrolyzed SiO$_2$ layer that is naturally occurring on the surface of silicon. [13]

Polyacrylic Acid (PAA) has been used with some success for silicon materials (first by Magasinski et al.) and it displays some similarities with NaCMC. The stiffness of dry NaCMC and PAA is similar (Young’s modulus of 4000 for PAA compared to 400 for PVDF) and although PVDF softens when in contact with electrolyte solvents, PAA (and NaCMC) do not soften significantly. The performance of NaCMC, PAA, and PVDF was tested showing that both NaCMC and PAA are improvements over PVDF and that PAA has a positive effect on the performance over that of NaCMC. It was also suggested that this was because of the high concentration of carboxylic groups on PAA. Polyvinyl acid (PVA) has also been proposed as a similar binder material for silicon anodes as well with limited success. [14, 15, 17]

A novel binder for silicon has also been explored recently utilizing a component of brown algae (alginate) in lieu of a polymeric binder. Kovalenko et al. demonstrated very stable performance of a nanosilicon electrode for 100 cycles using alginate as a binder material. The alginate binder also utilizes carboxylic groups to bind covalently to the silicon electrode materials. [16]

While these binder materials have all been studied with regards to silicon based anode materials, there is no common testing criteria or even material that could adequately predict the performance of each for a new material. It is notable that
in these studies, NaCMC shows improvement over PVDF but PAA and alginate have been shown to outperform both. It is also important to consider some of the shared characteristics of the more successful binders. Stiffer binders appear to be more successful at maintaining the structure of the electrode under the stresses of the silicon’s expansion as PAA and NaCMC demonstrate. Additionally the mechanism that attaches these binders to the silicon is a covalent bond formed by the carboxylic acid sites on the binder.

2.4 Solid Electrolyte Interface

The solid electrolyte interface (SEI) is extremely important for Si anodes. The SEI layer is formed because the negative electrode is cycling at low potentials where the electrolyte is unstable and the solvent and salt can be reduced and form a film on the surface of the electrode. This film can improve the electrode performance due to surface passivation. For a graphitic anode, the SEI layer forms and then remains (approximately) constant. Because of the constant expansion and contraction of the silicon particles as they charge and discharge, the SEI that forms is constantly being cracked apart during the lithiation and expansion of the particle. This exposes “clean” silicon and leads to the formation of additional SEI growth during each cycle. This uses Li$^+$ ions from the electrolyte and causes additional capacity loss. This also results in an extremely thick SEI layer that increases ionic resistance. [18, 19, 20]

2.5 Summary

Silicon and other alloying anode materials have been studied for the last few decades as a possible replacement for graphitic carbon anodes in lithium ion batteries. with the order of magnitude increase in theoretical capacity that it offers, silicon poses challenges to successful utilization as an anode material. It has been found that amorphous silicon helps overcome the initial irreversible capacity loss due to the energy required to break apart the crystallographic structure of crystalline silicon. Additionally, the particle size and morphology is extremely important to the cycling stability of the electrode. Multiple approaches to using the
stability and electrochemical performance of carbon to improve the silicon anode have been explored. Some of these structures are significantly complex or difficult to manufacture but they have produced notable improvements in electrode capacity and stability. Research has been done to find a binder material that would successfully accommodate or contain the volumetric expansion and contraction of silicon during electrochemical cycling.

In this thesis we will examine a simple and cost effective method to stabilize the performance of silicon using carbon in a systematic study of silicon to carbon ratios, binder materials and electrolyte additives.
Chapter 3

Material Preparation and Characterization

3.1 Methods and Materials

The primary components of the silicon-carbon nanocomposites are commercially available and thus readily attainable and relatively inexpensive. We used several commercially synthesized Silicon nanopowders including a Sigma Aldridge product with average diameter of $\leq 100$ nm and an Alfa Aesar product with an average diameter of $\leq 50$ nm. Super P® conductive carbon additive was purchased from TIMCAL America Inc. (USA). Binder materials were purchased from a variety of sources as powders and combined with DI water to form 1 wt% solutions unless otherwise noted.

All milling was done using a QM-3SP04 Planetary Ball Mill from Nanjing University Instrument Plant (China) with agate jars and milling balls of two sizes. Materials were characterized using X-ray diffraction using a Rigaku MiniFlex II powder X-ray diffractometer using Cu Kα radiation. Transmission electron microscopy was completed on a JEOL 1200 microscope at 200 keV. The electrochemical performance of the cells was characterized by galvanostatic cycling between 0.01 V and 1.5 V at room temperature using both Neware and Arbin multichannel battery test units. All rate and capacity calculations were based on the combined weight of the silicon and carbon excluding the binder content.
3.2 Battery Preparation

In order to create the silicon-carbon nanocomposite anode materials used in this research, silicon nanoparticles were milled with Super P® at 500 RPM to coat the Si with carbon. All samples were prepared by mechanical milling for one hour. The resulting silicon-carbon nanocomposite was then combined with the liquid binder solutions either by further mechanical milling or by extended stirring as indicated where appropriate to form a slurry. The slurries were spread onto a copper foil current collector and then dried in vacuum at 100°C for at least 8 hours. Individual circular electrodes with a diameter of 0.5 in. were then punched out of the foil and weighed to determine the mass of the active material on the electrode.

These electrodes were placed in a glove box (M Braun Labstar) with a argon atmosphere maintained with < 1 PPM H2O for assembly into CR2032 coin cells using lithium foil as the counter electrode and a separator membrane. The electrolytes used were based on 1 M LiPF6 in a 1:1:1 ratio mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) solvents. Additionally, some cells were tested with electrolytes containing 10% fluoroethylene carbonate (FEC) to improve the solid electrolyte interphase as detailed in Section 4.2.

3.3 Characterization of Prepared Materials

In order to confirm the composition of the milled silicon-carbon nanocomposites, they were tested via powder X-ray diffraction. All samples showed XRD peaks consistent with the silicon nanoparticles and with the conductive carbon as shown Figs. 3.2 and 3.3 which display no extraneous XRD peaks indicating unexpected contamination.

This fact, combined with TEM image in Fig. 3.1 of the milled nanocomposites showing the carbon additive coated onto the surface of the silicon nanoparticles leads to the conclusion that the carbon is coated onto the silicon nanoparticles but the lack of silicon carbide peaks in the XRD patterns means that the milling has only combined them mechanically rather than chemically bonding them. Fig. 3.1 also demonstrates that the milling process does not destroy or fracture the silicon nanoparticles as their spherical character is maintained.
Figure 3.1: TEM image of milled Si-C nanocomposite prepared from <50nm silicon nanoparticles milled with conductive carbon for one hour in planetary ball mill. Darker portions of the particles are the carbon coating. Scale bar is 100 nm
Figure 3.2: Powder X-ray Diffraction Pattern for Si-C nanocomposite material prepared by milling Alfa Aesar silicon nanoparticles and Super-P® carbon additive in a 4:5 ratio by weight for one hour in planetary ball mill.

Figure 3.3: Powder X-ray Diffraction Pattern for Si-C nanocomposite material prepared by milling Alfa Sigma Aldridge silicon nanoparticles and Super-P carbon additive in a 4:5 ratio by weight for five hours in planetary ball mill.
Chapter 4

Electrochemical Performance

This chapter outlines the process used to determine an ideal silicon-carbon nano-composite material that can be simply and relatively inexpensively produced utilizing a purely mechanical process. I have tested the effects of silicon nanoparticle size, Si:C ratio, binder, and electrode preparation method on the electrochemical performance and cycling stability of mechanically milled silicon-carbon nanocomposite electrode material. In order to evaluate the success of our materials, the paramount performance criteria used were gravimetric specific capacity and cycling stability. Therefore, once each material was produced via milling and a well-coated electrode was prepared from the slurry process, each sample was tested for its electrochemical performance over an extended number of cycles. Several runs of samples were completed with the goal of isolating and testing individual variables including nanoparticle size, ratio of silicon to carbon, binder materials, and electrolyte composition. With this focus we are able to optimize the performance of a mechanically milled silicon-carbon nanocomposite anode. In the following sections, the details of the testing for each parameter are presented and the results summarized.

4.1 Silicon Nanoparticle Size

A very important factor in the stability and performance of any silicon based anode is the morphology and size of the silicon particles or structures involved. As detailed in Section 2.1 there is a critical diameter \( D_c \) of \( \sim 150 \) nm above
Figure 4.1: TEM image of Alfa Aesar silicon nanoparticles as purchased with average particle size of < 50 nm. Size markers show the diameter of particles with only a (very) small minority of particles having a diameter larger than 120 nm. Scale bar is 500 nm.

which silicon nanoparticles show a distinct tendency to fracture apart during the lithiation driven expansion of the particles. [11, 34] In this work, we have been able to compare the performance of spherical silicon nanoparticles with advertised average diameters of < 100 nm and < 50 nm (Sigma Aldridge and Alfa Aesar respectively). Electrodes were prepared from milled 4:5 Si:C nanocomposite and
stirred with aqueous binder solution. The 4:5 Si:C ratio was chosen following pre-
liminary testing detailed in the following section. Figure 4.1 shows a TEM image
that demonstrates the range of particle sizes within the Alfa Aesar silicon. With
almost all particles well below the $D_c$ of $\sim 150$ nm, it is reasonable to assume that
the performance of this material would be relatively stable and it was proved via
electrochemical testing that, as predicted by these previous studies of silicon particle
size, the silicon nanoparticles with the smaller average diameter display better
capacity retention and rate capability. [11, 34] With the average particle size of the
Sigma Aldridge material in this study being much closer to $D_c$ there are enough
particles above 150 nm within the range of particles to add capacity deterioration
due to self fracturing to any addition physical pulverization of the anode due to
the expansion and contraction of the larger particles. Unless otherwise noted, all
further testing was done using the Alfa Aesar silicon nanoparticles.

4.2 Electrolyte Comparison

One of the first parameters examined was the effect of the electrolyte additive
fluoroethylene carbonate (FEC) on cycling stability. FEC has been investigated
as an electrolyte additive and has been found to improve the first cycle irreversible
capacity loss, reduce electrical impedance, and decrease capacity loss during cycling
when used with silicon based materials. The FEC results in thinner solid electrolyte
interface (SEI) layers on the surface of bare silicon. [35] For our silicon-carbon
nanocomposite material, it seems that the carbon is primarily dispersed onto the
silicon nanoparticles. Therefore it was necessary to consider the effect of FEC to
determine if it had the same effect or if the carbon additive rendered the FEC
unnecessary or possibly only marginally helpful.

We were able to perform parallel testing of identical electrodes using different
electrolyte solvent combinations in order to quantify the exact effect of the elec-
trolyte additives. These electrodes were from the same sample with similar masses
of active material on each and the coin cells used for testing were assembled at
the same time utilizing the same methodology and quantity of electrolyte in order
to ensure that any variance in the electrochemical performance would be due to
the electrolyte additive only. Both electrolytes were prepared in our lab and the
Figure 4.2: Comparison between 1 M LIPF₆ in EC:DEC:DMC (1:1:1) and 1 M LIPF₆ in EC:DEC:DMC:FEC (3:3:3:1) electrolytes. Cells were prepared by stirring binder with nanocomposite. The cells were cycled for 2 cycles @ 200 mA/g then 2 cycles @ 600 mA/g and then cycled at 1000 mA/g for the remainder of the testing.

The control electrolyte composition was prepared with 1 M LIPF₆ in a solvent mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) solvents in a 1:1:1 ratio. The FEC additive containing electrolyte was prepared similarly but with a different solvent mixture: 1 M LIPF₆ in a 3:3:3:1 ratio mixture of EC:DEC:DMC:FEC solvents.

Figure 4.2 shows the effect of 10% FEC in the electrolyte. The drastic improvement in cycling stability reflects the effect of FEC on SEI formation during cycling. This drastic improvement in performance: after 100 cycles the cell containing the FEC electrolyte still had a gravimetric specific capacity of close to 600 mAh/g while the control cell’s capacity had dropped to less than 100 mAh/g. This improvement justified the use of the electrolyte containing FEC throughout the testing of other parameters in this study.
4.3 Si:C Ratio

One of the most important parameters in this test is the ratio of silicon to carbon in the prepared materials. The higher the relative content of silicon, the higher the overall theoretical gravimetric energy density of the prepared material. However, the conductive carbon additive increases the conductivity and cyclic stability of the electrode material. With the known theoretical gravimetric energy density of silicon and negligible energy density of conductive carbon as a lithium ion battery anode material. We can use these to calculate a theoretical energy density for each electrode material. Initially, several ratios of silicon to carbon were chosen to test before continuing to test other parameters. A single ratio was needed to be a consistent control ratio for all of the other parameters. To this purpose, materials were first prepared and electrochemically cycled with the following four silicon to carbon ratios: 3:6, 4:5, 5:4, and 6:3. As shown in Table 4.1, the theoretical capacity of the 3:6 silicon to carbon ratio sample is merely a third of the theoretical capacity of silicon. This means that it is important to find the appropriate balance between the improved electrode stability offered by the conductive carbon additive and the theoretical capacity offered by the silicon nanoparticles in order to maximize the overall performance of the silicon-carbon nanocomposite material.

<table>
<thead>
<tr>
<th>Si : C Ratio</th>
<th>Approximate Theoretical Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 : 6</td>
<td>1336 mAh/g</td>
</tr>
<tr>
<td>4 : 5</td>
<td>1781 mAh/g</td>
</tr>
<tr>
<td>5 : 4</td>
<td>2226 mAh/g</td>
</tr>
<tr>
<td>6 : 3</td>
<td>2672 mAh/g</td>
</tr>
</tbody>
</table>

Table 4.1: Approximate theoretical gravimetric energy density using 4008 mAh/g for the gravimetric energy density of silicon and neglecting any contribution from the conductive carbon.

Initial testing was done to determine an appropriate ratio to use for other test parameters and of these four ratios, the 4:5 silicon-carbon ratio was found to offer the best performance. Later, additional ratios were tested to fill in the gaps between these ratios for greater accuracy in the optimization process. Results for the ratio testing are detailed below.

We have chosen Alfa Aesar silicon nanoparticles for all ratio testing and pre-
pared electrodes using the previously described methodology with all electrodes prepared from slurries that were stirred for 20–21 hours before coating onto copper foil and vacuum dried overnight. The ratios varied from 3:6 to 6:3 with five even steps in between for a total of seven samples to test. In this comparison, NaCMC was used as a control binder with 10 wt% of binder material in each electrode. Cells were prepared using electrolyte with 10% FEC added to improve cycling stability.

![Figure 4.3: Cycling data for Alfa Aesar Si-carbon nanocomposites with different Si:C ratios. Cycled between 0.01 and 1.0 V with 1 M LIPF6 in EC:DEC:DMC:FEC (3:3:3:1) electrolyte. The stabilizing effect of the conductive carbon is very clearly seen; the electrodes with the lowest carbon contents display the exponential decay in capacity common to pure silicon materials.](image)

These electrodes were then cycled between 0.01 V and 1.0 V with increasing charge discharge rates; the rate was kept at 200 mA/g for two cycles, then 600 mA/g for two cycles, and finally the remaining cycles were completed at a charge rate of 1000 mA/g. It is worth emphasizing the choice to use the weight of the
entire nanocomposite material (not just the silicon content) as the ultimate goal of this research is a functional anode material; comparing the samples on the basis of total weight allows for an evaluation of the prepared material rather than a comparison of the utilization of the silicon content as an individually calculated theoretical capacity based charging rate would produce. Figure 4.4 shows the coexisting trends of decreasing initial capacity with decreasing silicon content and increasing stability close to the 1:1 ratio of silicon to carbon.

![Figure 4.4: Revisualization of the data from Figure 4.3 comparing the gravimetric energy density of each electrode material at specific cycles through the first 100 cycles.](image)

The best cycling stability is exhibited by electrodes with a Si:C ratio of 1:1 (the sample labeled 9:9:2) as shown in Fig. 4.3. This is very close to the 4:5 ratio of silicon to carbon that the other parameters have been examined with. This is important to ensure the relevance of the other test results. Additionally, the proposed relationship between carbon content and cycling stability has been validated with these results. However, when we look at these same results in a different form as shown in Figure 4.4 we see that while the general connection between high silicon content and large initial capacity is upheld, there appears to be a decrease in cycling stability as the silicon content decreases below the optimum 1:1 ratio.
Figure 4.5: Data from Figure 4.3 corrected to show the gravimetric energy density based on the mass of silicon only for the 3:6:1, 9:9:2, and 6:3:1 ratios of Si:C:NaCMC. Note that the charging rates are based on the combined mass of silicon and carbon. Because of this, the charge-discharge rates for cycles 5-200 (1000mAh/g_{Si+C}) correspond to \sim 0.4 C for the silicon-carbon ratio of 6:3 but \sim 0.75 C for 3:6.

When we examine these results after correcting the gravimetric energy density to the mass of silicon only as shown in Figure 4.5 we can more clearly see that the increased cycling stability is not completely consistent with the increase in carbon content. This may be attributed to the charge discharge rates being based on the mass of the nanocomposite material while the theoretical capacity of the materials varies with the silicon-carbon ratio. This can be considered in terms of the C rates for each material; the cycling of these electrodes was done at \sim 0.4 C for the 6:3:1 electrode, \sim 0.45 C for the 9:9:2 electrode, and \sim 0.75 C for the 3:6:1 electrode. This makes some sense of the faster capacity loss of the 3:6:1 sample in this circumstance. However, because our concern is to optimize an electrode material with a high and stable specific capacity, the results shown in terms of the combined mass of silicon and carbon are the most relevant measures of success.
4.4 Binder Comparison

In this research, a multitude of binders were tested with the milled nanocomposite materials. These binders included the following materials and combinations: alginate, several chitosan based materials, carboxymethylcellulose (CMC), sodium-carboxymethylcellulose (NaCMC), polyacrylic acid (PAA), lithium polyacrylate (LiPAA), polyvinyl acid (PVA), 1:9 and 2:8 ratio mixtures of PVA:PAA, and xanthan gum. These binders were all tested with the basic 4:5 silicon-carbon sample used throughout this research as the baseline. The best performance with this material was achieved with PAA, LiPAA, and NaCMC and so these binders are included in this section. The other binder results were omitted for either poor performance or performance insufficient to match that of NaCMC. The performances of PAA and LiPAA are very similar and both materials are meaningful improvements over that of NaCMC. This is clearly shown in Figure 4.6 with very similar results for each.

![Figure 4.6: Cycling data for Alfa Aesar Si-carbon nanocomposites with different binders in a 4:5:1 ratio by weight of Si:C:Binder. Cycled between 0.01 and 1.0 V with 1 M LIPF6 in EC:DEC:DMC:FEC (3:3:3:1) electrolyte.](image)

Cells were also prepared from the same electrodes using electrolyte that contained no FEC additive in order to further test the validity of previous results in Section 4.2 as well as test for any unexpected result with the new binder materials.
The results (Figure 4.7) show that FEC is indeed vital to achieving stable cycling performance. With no FEC these same electrode materials display significant capacity degradation as well as showing some unexpected disconnects in performance. We will discuss some possible explanations for this in the next chapter.

Figure 4.7: Cycling data for Alfa Aesar Si-carbon nanocomposites with different binders. Cycled between 0.01 and 1.0 V with 1 M LIPF6 in EC:DEC:DMC (1:1:1) electrolyte.

4.5 Summary and Conclusions

We were able to test the effect of silicon particle size by using several different sizes of silicon nanoparticles; obtaining very good performance with particles with average diameter of less than 50 nm in the commercially available Alfa Aesar silicon nanoparticles. Si:C ratios were examined between 1:2 and 13:5 with an expected relationship between higher initial capacity with and higher silicon content. It was also determined that there is an optimum balance between silicon and carbon that yields a gravimetric specific capacity of approximately 1000 mAh/g after 150 cycles in the case of the 9:9:2 sample shown in Figure 4.3 at an effective charging rate of ~0.45 C. Additionally, we tested the performance of a variety of binder materials, coming to the conclusion that PAA or LiPAA provided the most stable
performance as shown in Figure 4.6. It was also determined that the presence of FEC in the electrolyte is extremely important for achieving relatively stable cycling for these silicon-carbon nanocomposite materials.
Chapter 5

Ex-Situ Study SEM / Mechanical Failure of Electrode Material

In the preceding chapter we tested anode materials, binders, and electrolyte solely according to their electrochemical performance. Further examination of the electrode deterioration that corresponds to the deterioration of the electrode’s capacity when cycled with different electrolytes. In order to view the effect of cycling a silicon-carbon electrode (prepared as described in section 3.2) with and without FEC as an electrolyte additive on the mechanical integrity of the anode material, we used high resolution SEM to view the structure of the electrodes in its pristine state as well as its condition post cycling with different electrolytes after one and ten cycles. The following sections detail the methodology for this procedure as well as showing the resulting electrode degradation using SEM images and the charge-discharge curves produced during electrochemical cycling of the electrodes.

5.1 Methodology

Electrodes were prepared using a 4:5 Si:C ratio with 10 wt% NaCMC as the binder and the slurries were mixed by stirring for 20 hours and then spread and dried in vacuum ovens per the standard methodology described in Chapter 3. All samples in this test were taken from the same electrode foil. The pristine sample was placed in the HR-SEM with no additional preparation. The post cycling samples were all prepared in coin cells with electrolyte made up of 1M LiPF6 in three
different solvent mixtures: a 1:1:1 ratio mixture of EC, DEC, and DMC with no additives and then two samples with 10 % FEC by volume. Two cells were prepared with each of the electrolytes. One cell with each electrolyte was cycled once and the other was cycled for ten charge-discharge cycles before being carefully disassembled and washed with EC repeatedly. The remaining solvent was then allowed to evaporate in vacuum before being carefully prepared for SEM imaging. This process was done delicately to avoid any mechanical stress on the electrode. In order to achieve full delithiation of the samples prior to SEM imaging, the samples were maintained at zero voltage for at least two hours before disassembly allowing any residual lithium to discharge from the electrode. No discoloration was observed during the disassembly or washing processes indicating that the material was sufficiently delithiated to prevent any reaction when exposed to air.

Figure 5.1: HR-SEM image of pristine 4:5:1 Si:C:NaCMC electrode.
5.2 Initial Condition of Electrode

Figure 5.1 shows the surface structure of the pristine electrode via SEM imaging. The structure of the silicon nanoparticles is the clearly visible dominant structure of the electrode. It is also notable that the NaCMC binder appears to be evenly distributed over the materials. This provides a point of comparison for the post cycling samples in the following sections.

5.3 Cycling with Basic Electrolyte

After carefully disassembling the cells after cycling, the electrodes themselves were washed with EC and while the electrodes cycled with FEC were very similar in appearance to that of a pristine electrode, the electrode cycled for ten cycles without FEC showed significant damage. Images 5.2a and 5.2b show the electrode cycled in the basic electrolyte after one cycle and there is no appreciable destruction of the electrode material. Images 5.2c and 5.2d are after ten cycles and the electrode has undergone significant destruction resulting in large sections of the electrode material flaking away from the copper current collector. Approximately one third to one half of the electrode flaked away from the copper current collector after ten cycles. In the coin cell these sections could possibly still be in electrical contact with the copper current collector but it is likely that this large scale mechanical destruction of the electrode is the direct cause of the deterioration of the electrode’s capacity. The disconnects in the capacity shown in Figure 4.7 could possibly relate to large sections of the electrode becoming electrically stranded. This cannot be definitively proven by the data here, but it does provide a possible explanation for the electrochemical cycling data.

5.4 Cycling with FEC Electrolyte

These electrodes were cycled with the electrolyte containing FEC that has been shown to greatly improve electrochemical performance for silicon based electrode materials including the mechanically milled silicon-carbon nanocomposite tested in this research. The high resolution SEM imagery of the electrodes after cycling
Figure 5.2: High resolution SEM images of 4:5:1 Si:C:NaCMC electrode after cycling in electrolyte consisting of 1 M LiPF₆ in a 1:1:1 ratio mixture of EC:DEC:DMC solvent. The SEI layer is visible in 5.2b and 5.2d as a slight layer over the material.
show that the effect the FEC has upon the SEI layer formation and composition has a stabilizing effect on the electrode as a whole.

Images 5.3a and 5.3b are after one cycle and as in the basic electrode example there is no appreciable destruction of the electrode material. The contrast to the electrode cycled without the FEC additive is much more drastic after ten cycles. Images 5.3c and 5.2d show that after ten cycles in the electrolyte containing FEC, there is no significant large scale destruction of the electrode. In 5.3c there is only some slight cracking that appears to be similar to the electrode after one cycle. The visible SEI layer in 5.2d and 5.2d has a noticeably different appearance (presumably reflecting the effect of the FEC on the formation of the SEI layer. The electrochemical effect of the FEC additive on performance was further discussed in Section 4.2, and the ex situ SEM imagery shows that there is a direct mechanical mechanism that affects the electrode’s physical integrity and from that the electrochemical stability.
(a) HR-SEM image of electrode after one cycle with FEC electrolyte. Scale bar is 100 µm.

(b) HR-SEM image of electrode after one cycle with FEC electrolyte (high magnification). Scale bar is 500 nm.

(c) HR-SEM image of electrode after ten cycles with FEC electrolyte. Scale bar is 100 µm.

(d) HR-SEM image of electrode after ten cycles with FEC electrolyte (high magnification). Scale bar is 500 nm.

Figure 5.3: High resolution SEM images of 4:5:1 Si:C:NaCMC electrode after cycling in electrolyte consisting of 1 M LiPF$_6$ in a 3:3:3:1 ratio mixture of EC:DEC:DMC:FEC solvent.
Chapter 6

Conclusion

6.1 Conclusions

Silicon has been examined for several decades as a possible replacement for the current commercial standard anode material: graphitic carbon. With an order of magnitude improvement in theoretical capacity, silicon is appealing as an improved material. However, research has focussed on methods of mitigating silicon’s shortcomings as an anode material. This thesis has examined the performance of an easily produced silicon-carbon nanocomposite material that is made using only commercially available materials and is easily produced using a one-step mechanical milling process in which the silicon and conductive carbon additive (Super P® from TIMCAL America Inc.) are mechanically milled together to disperse the carbon onto the silicon. Isolating and testing individual parameters that are important to the performance of the nanocomposite material enabled us to perform a systematic study of the factors that control the performance of this silicon-based anode material. Several important factors were examined to provide initial guidance that was necessary to streamline the examination of other parameters. Firstly, the effect of silicon nanoparticle size was examined following the guidance of previous studies on silicon particle size and self-fracturing during lithiation and delithiation. With this result, we chose commercially available silicon nanoparticles from Alfa Aesar with an average particle size of $\leq 50$ nm. With almost all particles in this product $\leq 120$ nm as confirmed by TEM microscopy, this material was under the proposed critical diameter for self-fracturing as determined by Liu.
et al. [34]

With the silicon nanoparticle component determined, the next step was to determine the best electrolyte to test a silicon based anode material and the performance of the electrolyte additive fluoroethylene carbonate (FEC). Performance tests using several different binders confirmed previous results that assert that the FEC has a positive effect on the cycling stability of silicon anodes. The proposed mechanism for this improvement is directly related to the effect of FEC on the formation of the solid electrolyte interface layer (SEI). High resolution SEM imagery of ex situ, cycled electrodes further supported the assertions that FEC improves the stability of the anode during cycling.

One of the most important elements of this study is the systematic examination of the effects of silicon-carbon ratio on the capacity and cycling stability of the produced electrode. A ratio of 1:1 was determined to offer the optimal balance of initial capacity from a high silicon content with the stabilizing effects of the conductive carbon additive. At this ratio, an anode was able to achieve a capacity of nearly 1000 mAh/g after 150 cycles.

Finally, electrodes were prepared using alternative binder materials to optimize this important component of the electrode. Silicon’s extreme expansion during the lithiation process puts extreme strain upon the electrode’s structure. The common PVDF binder utilized for many cathodes and graphitic anodes has been shown to be insufficient to maintain the structure (and thus the performance) of the anode. Sodium-carboxymethylcellulose (NaCMC) was used as a common baseline material throughout this study and polyacrylic acid (PAA) and lithium polyacrylate (LiPAA) were determined to offer valuable improvements in electrochemical performance.

6.2 Future Work

While this study has found several optimal components and compositions for a silicon-carbon nanocomposite anode material that is simple and inexpensive, there is still further research to be done. The effect of FEC in the electrolyte was definitive but the precise mechanism with which this is accomplished is still unclear. The exact composition of the SEI layer that is formed when silicon is cycled utilizing
electrolyte containing FEC could offer insight into methods of further improving the stability of the electrode by improving the SEI layer’s composition. Additionally, further optimization of the exact silicon carbon ratio utilizing LiPAA and PAA as binders would be able to determine if there is an alternate ratio of silicon to carbon that is optimal for these different binders.
Bibliography


