ABSTRACT

FU, KUN. Advanced Structural Electrode Materials for Lithium-Ion Batteries and Lithium-Sulfur Batteries. (Under the direction of Drs. Xiangwu Zhang and Philip D. Bradford).

Batteries, as one of the most appropriate and promising electrical energy storage systems, are playing a vital role in future use of electrical energy. Significant efforts have been placed on exploring high specific capacity electrode for advanced lithium based batteries, including lithium-ion batteries and lithium-sulfur batteries.

Lithium-ion batteries and lithium-sulfur batteries are two distinguishing energy storage systems that have different energy storage mechanisms. Rechargeable lithium-on batteries have two \( \text{Li}^+ \) intercalation electrodes, in which the electrical and chemical energies are interconverted via a reversible \( \text{Li}^+ \) intercalation/de-intercalation process between the electrodes. Rechargeable lithium-sulfur batteries operate by reducing elemental sulfur in the discharge process to produce a series of soluble lithium polysulfides to ultimately form solid lithium sulfide and converting lithium sulfide back to elemental sulfur in the charge process.

For lithium-ion batteries, the research focused on the use of silicon as an anode material since it has the highest theoretical capacity of 4200 mAh/g, which is four times higher than that of graphite (375 mAh/g). Silicon has the greatest potential to replace graphite for use in next-generation lithium ion batteries. However, challenges from its semi-conductive property and the huge volume expansion (300%) during the lithiation process greatly hinder silicon’s application into lithium-ion batteries. The study of how to harness silicon into an electrode with superior chemical performance has been one of the driving factors for this work. Gaining this understanding in regards to silicon may also provide potential processing routes to other
active materials, sensitive to volume change in lithium-ion batteries. In this work, silicon and carbon composites, including silicon-carbon nanofibers and silicon-carbon nanotubes, were designed and developed to try to solve the problems caused by the silicon volume expansion, enabling a specific capacity of more than 1000 mAh/g as a promising anode materials for lithium-ion batteries.

In addition to lithium-ion batteries, advanced cathode design of lithium-sulfur batteries was studied and discussed. The motivations for studying lithium-sulfur batteries come from two most important merits of sulfur: (a) abundance and low cost, and (b) high capacity of 1675 mAh/g. Lithium-sulfur batteries have a 3~5 fold higher theoretical energy density than conventional lithium-ion batteries. For sulfur cathodes, the main barriers to commercial production are their short cycle life, low charging efficiency, and high self-discharge rate, which are caused by the non-conductivity of sulfur and the migration of the dissolved sulfur reduction products out of the cathode region. Therefore, the electrochemical properties of sulfur and its cathode structures deserve investigations and discussions in this work. An advanced sulfur electrode was firstly developed and studied in my work, which exhibited a good cycling performance with a high sulfur loading (2.6 mg/cm²) and high sulfur content (65%) as cathodes for lithium-sulfur batteries.
Advanced Structural Electrode Materials for Lithium-Ion Batteries and Lithium-Sulfur Batteries

by
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DEDICATION

To my beloved mother, father and all my family members,
without those love, guidance and support, this would not have been possible.

I appreciate to have you all in my life.
BIOGRAPHY

Kun Fu received his Bachelor degree in Textile Science and Engineering at Donghua University in 2009 and his master degree in Textile Engineering at Philadelphia University in 2011. He came to North Carolina State University and enrolled in the Fiber and Polymer Science Doctoral program in August 2010.
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CHAPTER 1 INTRODUCTION

Lithium ion batteries and lithium sulfur batteries are two important electrical energy storage systems. The pursuit of batteries for high performance will never end and it keeps motivating us to find high-energy-density electrode materials for advanced lithium batteries. The capacity of a cell largely depends on the specific capacity of electrode materials. Therefore, it is important to design and develop high-performance electrodes for advanced lithium batteries.

For lithium ion batteries, silicon has the highest capacity of 4200 mAh/g, which is four times higher than that of graphite (375 mAh/g). It has the greatest potential to take the place of graphite for the next-generation lithium ion batteries. However, challenges from its semi-conductive property and the huge volume expansion (300%) during the lithiation process greatly hinder silicon’s application into lithium ion batteries. The study of how to harness silicon into an electrode with superior chemical performance has been one of the driving factors for this work. Gaining this understanding in regards to silicon may also provide potential processing routes to other active materials, sensitive to volume change in lithium ion batteries.

In addition to lithium ion batteries, advanced cathode design of lithium sulfur batteries will be studied and discussed in this work. The motivations for studying lithium sulfur come from two most important merits of sulfur: (a) abundance and low cost and (b) high capacity of 1675 mAh/g. Lithium sulfur battery have a 3~5 fold higher theoretical energy density than conventional lithium ion battery. Recently, some researchers have moved from studying
lithium ion batteries to lithium sulfur batteries, as seen by an increasing number of publications in the scientific literature. For the sulfur cathode, the main barriers to commercial production are the non-conductivity of sulfur and the migration of the dissolved sulfur reduction products out of the cathode region. For the lithium sulfur batteries, problems include short cycle life, low charging efficiency, and high self-discharge rate. Therefore, the electrochemical properties of sulfur and its cathode structures deserve systematical investigations and discussions in this work. An advanced sulfur electrode will be firstly developed and studied in my work.

The objective of this research is to understand the electrochemical and structural evolution properties of silicon and sulfur materials then to design and fabricate electrodes for lithium ion and lithium sulfur batteries, respectively. In this research, different carbon scaffolds will be synthesized and combined with silicon and sulfur in unique nanostructures to better understand their composite behavior in lithium ion and lithium sulfur batteries. The carbon scaffolds included carbon nanofiber mats and super-aligned carbon nanotube sheets. Incorporation of silicon in the form of nanoparticles and conformal coatings was studied in lithium ion batteries. A new method of sulfur deposition on the carbon scaffolds was studied in the lithium sulfur batteries.
CHAPTER 2 LITERATURE REVIEW

2.1 Electrochemical batteries

The concerns of environmental issues and limited fossil fuels have attracted great interests in generating cleaner electricity from the renewable sources, including solar, ocean wave, and wind. To harvest these renewable energies effectively and use this energy widely in transportation applications, electrochemical energy storage (EES) is very necessary to efficiently store the intermittent renewable electricity and reduce the waste emission from the traditional transportation methods. Therefore, EES has, and will continue to become a very important and indispensable component for the future energy system.

Electrochemical energy storage is classified into two classes: batteries and super-capacitors. Batteries are normally feature high energy density and stable operating voltage and are further divided into primary and rechargeable batteries. Super-capacitors feature high power and a sloping operating voltage and are further divided into electrochemical double-layer capacitor and pseudo-capacitors. It should be mentioned that all of these storage systems utilize a faradaic process for energy storage, except for the double-layer capacitor which stores energy by physically capturing the opposite charges on electrode surfaces.

The physical structure of an electrochemical battery consists of two electrodes, a separator, and electrolyte. The electrolyte can be a liquid or a solid. Solid electrolytes are used with
gaseous or liquid electrodes; they also can be used with solid electrodes, but solid-solid interfaces have poor ionic transfer kinetics unless the solid electrolyte is a polymer or thin solid electrode.\textsuperscript{3} The separator is used to keep the solid electrodes apart to prevent a short circuit and allow liquid electrolyte to transfer though its porous structure.

The schematic of the relative electron energies of electrodes and electrolyte in a thermodynamically stable battery is shown in Figure \textit{1}.\textsuperscript{4} The anode and cathode are reductant and oxidant with electrochemical potentials $\mu_A$ and $\mu_C$, respectively. The energy gap of liquid electrolyte is $E_g$, which is the window of the electrolyte between its lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO).\textsuperscript{4} A $\mu_A$ above the LUMO will reduce the electrolyte unless a passivation layer is formed to block the electron transfer; a $\mu_C$ below the HOMO will oxide the electrolyte unless the electron transfer is blocked.\textsuperscript{4} Therefore, a thermodynamically stable battery should have its anode and cathode located within the potential window of the electrolyte, which constrains the battery’s open-circuit voltage $V_{oc}$ as

$$ e V_{oc} = \mu_A - \mu_C \leq E_g \quad (1) $$

where $e$ is the magnitude of electron charge.
In the discharge step, electrons move from the anode via an external circuit to the cathode. To neutralize the negative charged cathode, cations are released from the anode via the electrolyte to the anode. In the charge step, the whole process is reversed, which makes it a rechargeable battery. In a thermodynamic equilibrium, the magnitude of the electronic current in the external circuit must be matched with the internal ionic current through electrolyte. Due to fact that the ionic current is much smaller than the electronic current density, kinetics necessitate that a relatively longer time to reach equilibrium is needed, leading to a lower capacity than its theoretical capacity.

For a battery, energy density is a basic criteria to evaluate the performance. The energy density of a battery depends on the capacity of reversible charge transfer per unit weight (mAh/g) and
the open-circuit voltage. A higher voltage and higher capacity of electrodes are desired for higher energy density. Therefore, to design a high energy density electrochemical battery, one must (a) find an electrolyte having a wide potential window range, and (b) choose appropriate anode and cathode materials with their $\mu_A$ and $\mu_B$ matched well to the electrolyte potential window and (c) design structural electrode to maximize their electrochemical performance in battery systems.$^4$

In this review, we will focusing on the structural electrode design, especially on the anode and cathode for lithium ion and lithium sulfur batteries, respectively.

2.2 Introduction of lithium ion and lithium sulfur batteries

2.2.1 Brief introduction of lithium ion batteries

*The birth of lithium ion batteries*

In 1981, Akira Yoshino, a Japanese chemist, started research on a nonaqueous secondary battery using polyacetylene as the negative electrode. In 1983, he fabricated a first prototype rechargeable battery by using lithium cobalt oxide (LiCoO$_2$) as the cathode and polyacetylene as the anode. The concept of lithium ion battery was first introduced. Yoshino believed that the positive electrode material should be a transition-metal oxide to providing lithium ions for the negative electrode during charging. This idea was first confirmed by operation in a sealed glass test tube, as shown in Figure 2.$^5$ This test-tube cell is the direct precursor of the modern
lithium ion battery and it functioned with the same cell reaction and operating principle as the existing lithium-ion batteries today.\textsuperscript{5}

**Figure 2.** The first test tube cell of lithium ion battery.\textsuperscript{5}

Due to the low density of polyacetylene, Yoshino switched to carbonaceous materials as the anode material and successfully fabricated the first prototype of practical lithium-ion battery, by using LiCoO\textsubscript{2} as the cathode and carbonaceous materials as the anode which enabled stable charging and discharging over many cycles for a long period of time.\textsuperscript{5} Starting at that point, modern lithium-ion battery were introduced to the world.

*Mechanism of lithium ion batteries*

A typical lithium ion battery is show in **Figure 3.**\textsuperscript{6} During charging, lithium ions are produced from the layered LiCoO\textsubscript{2} cathode, pass across the electrolyte, and then intercalate into the graphite layers in the anode. Upon discharging, lithium ions leave the graphite layers, transferring through the electrolyte, and then intercalate back into the layered cathode.
Figure 3. Schematic of a lithium ion battery.\textsuperscript{6}

Their chemical reactions are described as below:

\begin{align*}
\text{Cathode: } & \text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \quad (2) \\
\text{Anode: } & 6\text{C} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{C}_6 \quad (3)
\end{align*}

Motivation of nano-structural design for electrodes of lithium ion batteries

1. Nanostructures can increase the rate of lithium insertion and de-insertion of the electrode due to the short lithium ion diffusion distance within active materials.\textsuperscript{6,7}

2. Nanostructures can improve the electrical conductivity of the electrode because of the shortened electron transport pathway.\textsuperscript{6,7}

3. Nanostructures can enhance the ionic conductivity of the electrode since the high surface area allows sufficient contact area with the electrolyte.\textsuperscript{6,7}
2.2.2 Brief introduction of lithium sulfur batteries

Motivation of the transition from lithium-ion batteries to lithium-sulfur batteries

Conventional lithium ion batteries have cathodes with crystalline structures, featuring both electronic and ionic conductivity and the ability to reversibly (de)insert lithium ions with minimal structural change. The current cathode crystal materials have reached their theoretical capacity limits and may not be able to sufficiently meet the transport applications needs in the future. To produce higher energy density batteries with lower cost, new battery systems are being sought to outperform current lithium ion battery chemistries.

Due to the abundance and low cost of elemental sulfur, lithium sulfur batteries have been considered as a promising high energy density battery system. The overall redox reaction is given as:

\[ S_8 + 16 \text{Li} \leftrightarrow 8\text{Li}_2S_8 \] 

(4)

The average voltage of lithium sulfur batteries is around 2.15 V with respect to Li⁺/Li, which is lower than 3.8 V of lithium ion batteries. Although lithium sulfur batteries have a lower voltage, their high capacity around 1672 mA/y/g offsets the low voltage and can still exhibit a high energy density of 2500 Wh/kg or 2800 Wh/L on the basis of weight or volume, respectively.\(^8\) Thus, lithium sulfur batteries have been developed into a new energy storage system beyond lithium ion batteries.
Basic properties of sulfur

Sulfur is the 17th most abundant element in the Earth and in nature, and the most common sulfur is in the form of cyclic octasulfur (S₈). Octasulfur has three forms: α-sulfur, β-sulfur, and γ-sulfur. The latter two are metastable and can convert to α-sulfur in storage at ambient temperature. The α-sulfur has a melting point at 115.21°C and boiling point at 444.6°C. In the melted state, the viscosity slowly decreases to its lowest viscosity at 150°C, and then a remarkable increase at 160°C as a result of the opening and polymerization of the octasulfur rings until 190°C at which the viscosity decrease because of the depolymerization of sulfur. This unique viscosity-temperature behavior can be applied to the impregnation of sulfur into the porous carbon structures for the sulfur-carbon electrode.¹

Mechanism of lithium sulfur batteries

The schematic of a typical Li-S cell and its ideal charge-discharge profile are shown in Figure 4.⁹ Lithium metal is used as the anode and elemental sulfur is used as the cathode. During the discharge, the solid octasulfur is reduced to a dissolved low-order polysulfide and consequently to solid Li₂S₂ and Li₂S. In the charge process, the solid Li₂S₂ and Li₂S will be oxidized to solid octasulfur in the reverse steps.
Figure 4. Schematic of a lithium sulfur battery and its ideal charge-discharge profile.\(^9\)

*Challenges of sulfur cathodes*

1. Low conductivity of sulfur and its reduction products.\(^9\)

2. The dissolution of polysulfide out of cathode region, causing the loss of sulfur active materials.\(^1\)

3. Migration of polysulfide between cathode and anode regions.\(^8\)

4. Need of high sulfur content and sulfur loading.\(^1\)
2.3 Polymeric binders for lithium-ion batteries

In this chapter, the basic information of polymeric binders and their requirements for use in batteries are reviewed. The cooperation between binders with active materials and current collector is reviewed and discussed. Finally, traditional and newly discovered binders are reviewed and compared.

2.3.1 Basic information of binders for use in batteries

Binder is an important component in composite electrodes in addition to other inactive materials such as conducting agents and current collectors. Binder plays an essential role in maintaining the mechanical stability of the electrodes. The electrochemical properties of active materials are significantly depending on the binder system that is required to maintain high electronic conductivity, mechanical binding, ductility, and electrolyte uptake. Therefore, an efficient binder is critical to the design of high performance battery systems.

Basic functions of binders

The foremost important property of binder is the binding capability with active materials and current collector to ensure the electronic and mechanical integrity of electrodes. Binders should preserve their binding performance without being impaired by the high polar electrolyte environment in batteries. They must be stable in electrochemical conditions of batteries and survive the repeating volume change of electrode materials during charging and discharging.
of battery. To design a binder which can accommodate the severe volume expansion of electrode materials is essential to maintaining the electrode integrity.

![Diagram of Si composite electrode during lithiation and delithiation process.](image)

**Figure 5.** Volume change of Si composite electrode during lithiation and delithiation process.

A traditional composite electrode is shown in **Figure 5.** Polymer binders and conducting agents consist of the binder system. Polyvinylidene fluoride (PVdF) as polymer binder is used to mechanically bond the active materials and conducting agents together to the current collector. Carbon black (CB) as conducting agent is to provide the electron pathway to active materials through current collector. This binder system is required to exhibit dual-functions: mechanical adhesion and electrical connection. In addition to the basic functions, the polymer covering the active materials needs to provide enough ionic conductivity by means of swelling in electrolyte. The swelling in the electrode should not compromise the mechanical bonding and electrical conducting of polymer binder system.

For Si composite electrodes, significant volume change expansion by up to 300% upon the fully lithiation of Si deteriorates the structural integrity of the electrode. Cracks and pulverization of Si continually damage its connection with the binder system. Consequently, the interfacial contacts between Si and conducting agents are weakened. Also, the electrode
film can lose contact with current collector by peeling off during cycling and electron pathway will be cut off, leading to fast capacity decay of the Si electrode. Thus, to design a binder or binder system with good mechanical bonding and electrical conducting is very essential to preserving Si or other electrode materials with large volume changes, so as to achieve good cycling performance of batteries.

**Requirements of binders for electrodes**

**Electrochemical stability**

As an inactive material in the electrode, the binder must survive in the highly polar carbonate organic electrolyte of lithium ion batteries. The chemical structures should be stable in electrochemical environment. PVdF is so far the most stable polymer for binders in lithium-ion batteries. PVdF is widely used as binders for cathode materials. This is because PVdF has good oxidative resistance to the reactive oxygen produced from metal oxides of cathode materials. The theoretical calculations by molecular orbital method determine the oxidation potential values of polypropylene (PE), PVdF, and polytetrafluoroethylene (PTFE) are -12.12 eV, -14.08 eV, and -15.47 eV, respectively. Compared to the oxidation potential of organic solvent EC (-12.46 eV) and PC (-12.33 eV), fluorinated polymers show higher resistance to oxidation.\textsuperscript{11} For the fluorinated polymers, the partially fluorinated PVdF is more stable and hard to be reduced compared to PTFE or fluorinated polymers containing hexafluoropropylene (HFP, -CF\textsubscript{2}-CF(CF\textsubscript{3})-).\textsuperscript{11}
Mechanical strength

Polymer binders are required to have strong adhesive properties adhering with active materials and conducting agents together to form a continuous and robust electron pathway. When choosing polymer binders, we need to consider the electrochemical behaviors of active materials used in composite electrode. For the cathode materials, electrical conducting pathway is the primary issue for making electrodes since they do not suffer from the volume expansion issue during charging and discharging. Hence, the mechanical stress and strain of PVdF is acceptable for bonding cathode materials and conducting agents. However, for most anode materials (e.g. silicon, germanium, tin), volume expansion and contraction occur during the lithiation and delithiation processes, leading to the isolation of active materials from the binder system. Thus, it is necessary to have some polymer binders with high mechanical strength and strain to constrain the volume change of the electrode. A series of polymers, such as alginate,12 carboxymethyl cellulose (CMC),13 polyacrylic acid (PAA),14 polyamide imide (PAI),15 polyacrylonitrile (PAN),16 have been investigated for use as battery binders. These polymers have higher mechanical properties compared to PVdF and perform better than PVdF as binders in electrodes.

Recent studies have indicated that the rigidity of polymer backbone played an important role in retaining the capacity of anode materials. Inspired by this point, three-dimensionally interconnected polymer binder is created by forming a cross-linked structure through the condensation reaction of PAA and CMC (as shown in Figure 6).17 The cross-linked polymers show high mechanical strength and Young’s modulus with non-recoverable deformation (in
Figure 7. The robust binder has less swelling in the electrolytes which can prevent the isolation of active materials and maintain the Si-binder interfacial bonding strength in the electrochemical environment.\(^\text{17}\)

![Figure 6. Schematic of Si-based anodes with PVdF and cross-linked polymer.\(^\text{17}\)](image)

![Figure 7. Expected typical stress-strain curves for PVdF and cross-linked polymer binders.\(^\text{17}\)](image)
A polymer binder system is basically a mixture of a polymer and dispersion medium. The medium can be organic solvent or water, depending on the soluble properties of polymers. A uniform and stable paste is prepared by mixing polymer binder with active materials and conducting agents. After being coated on current collector, the binder system should have good heat resistance under the heating rollers (200°C) during the manufacture of electrodes. Good adhesion is required for the binder to have strong bonding with active materials and current collector. Figure 8 shows the true density and apparent density of electrode active materials. All binders must be adjusted to appropriate values according to their applications in cathode or anode electrodes. Therefore, for a binder system to exert its best functionality in electrodes, specific optimized conditions (content, viscosity, composition, thickness of coating, porosity, pressing pressure, and heating rate and temperature) need to be carefully considered in the real case.

Figure 8. True density and apparent density of electrode active materials.
2.3.2 Understanding the role of binders in electrodes

*Cooperation between active materials, polymer binders, and conducting agents*

Active materials and inactive materials (polymer binders and conducting agents) make up the composite structure of electrode. To achieve high energy density, the active material should take up as much as possible in the composition of composite electrode and meanwhile inactive binder system at the least amount to provide sufficient electron transport and mechanical integrity. For an electrode, electrical conductivity is a critical factor to guarantee the functionality of active materials. An example of electrode composition is 90%, 4%, and 6% for active material, conducting agent, and polymer binder, respectively. Therefore, electrodes are special polymer-based composites which require high content of active material and low concentration of polymer.

It has been reported that bulk polymers behave different physical states when they are on a particle surface (*Figure 9*). Free polymer is the bulk polymer having no contact with active materials or conducting agents. Bound polymer (1-5 nm thick) is formed on the particle surface by chemical bonding or physical interaction due to the dangling surface bonds. The polymer chains within bound polymer tend to stiffly align with the surface, leading to the drastically physical properties change. Immobilized polymer is formed as an interfacial layer between the bound and free polymers. Due to the fixed polymer chains in bound polymer layer, both bound and immobilized layers stay amorphous even if the bulk polymer is crystalline. Because of the high concentration of active material in composite electrode, polymer binder can be mostly in the fixed state, leaving with small free polymers. This amorphous polymer
layer can absorb Li\(^+\) in the favor of ion conductivity and meanwhile accommodate volume changes during cycling. To maximize the energy density of the electrode, it becomes important to minimize the free polymer and control the fixed polymer on particles by tailoring electrode composition.

![Diagram of polymer states](image)

**Figure 9.** Three different physical states of polymer chains when they are close to the surface of particles.\(^{22}\)

The amount of fixed polymer is determined by the surface area and surface property of active materials and conducting agents. Due to the different surface chemistry and specific area, active material and conducting agent will compete for polymer binder and different fixed polymer layer forms on the surface of each component.

In a practical binder system, polymer binder forms a fixed layer on conducting agent and excess polymer binder forms free domains. When the active material is introduced into the binder system, a new fixed layer will be formed on the active material and the original free polymer domains will be squeezed as well (**Figure 10**).\(^{22}\) So the electrical conductivity of the binder
system will be changed accordingly. Therefore, the fixed polymer and free polymer need to be well optimized without compromising the electrical conductivity to meet the requirement of the electrode with high concentration of active material and low content of binder system in the electrode. Figure 10 d-e shows the abundant and deficient polymer binders in the composite, respectively. Liu et al developed a model to investigate the influence of composition on electrical conductivity of bulk electrode. Their experimental and modeling results are shown in Figure 11.

**Figure 10.** Schematic of the formation of fixed polymers on active material and conducting agent. (a) AM particle. (b) AB/PVDF matrix. (c) Mixed AM/AB/PVDF. (d) There is enough polymer binder to form fixed layers on both AM and AB. (e) There is a deficiency of polymer binder to form the fixed layer on AM and AB.
Figure 11 Experimental results (open symbol) and modeling results (solid symbol) of the electrical conductivity of different compositions of the composite electrode.\textsuperscript{22}

As shown in Figure 12, the schematic and SEM images of electrode with two extreme ratios of conducting agent and binder can be used to demonstrate the distribution of polymer binder in the electrode composite.\textsuperscript{22} For the high content of PVdF in the binder system, there are free polymer domains in the composite. More active materials will be bonded in matrix and good adhesion properties and mechanical stability will be obtained. However, these free domains will increase the Li\textsuperscript{+} transfer resistance at interfacial space. For the low content of PVdF in the binder system, conducting agents compete with the active material for the fixed polymer and there is no free polymer is in such low PVdF-containing composite, which can help to decrease interfacial impedance in the electrode. With the decrease in the concentration of active materials, agglomerated conducting agents surrounded by fixed polymer will cover the active materials to make sure that the effective area or Li\textsuperscript{+} transport extends to the entire surface of active materials.\textsuperscript{22} Therefore, different composition will meet different requirement of
batteries. In order to maximize the energy density, the best composition to accommodate high concentration of active material is the higher polymer and conducting agent ratio to ensure good adhesion and acceptable interfacial impedance; if power performance is the first concern, the composite can have low active material loading with lower polymer and conducting agent ratio to make high power electrode with the sacrifice of energy density.

Figure 12. Schematic and SEM images of binder distribution at different composition. AB:PVDF = 0.2:1 at high AM loading (a) and low AM loading (b); AB:PVDF = 0.8:1 at high AM loading (c) and low AM loading (d). Scale bar is 20 \( \mu \text{m} \).

2.3.3 Binder systems for Si nanoparticles

For Si-based electrodes, Si experiences a large volume change (>300%) during its lithiation process. The volume change brings cracks and pulverization as well as electrode failure during cycling. This structural change leads to unstable solid-electrolyte-interphase (SEI), causing continuous Li\(^+\) consumption, increasing electronic resistance and decreasing coulombic efficiency (CE) for each cycle. To achieve commercially viable Si-based electrodes, functional binders provide effective ways to overcome those challenges brought by the volume change of
Si. Therefore, it becomes necessary and important to study some special properties of polymer binders affecting the electrochemical performance of Si-based electrodes, guiding us to find and design more suitable binders for Si.

**Si-binder interactions**

The interaction between Si and binder plays an important role in holding Si particles and preventing the electrode from disintegration. Recently, results have shown that polymers with side functional groups, such as carboxylic acid, can have excellent bonding behavior with Si.\(^{12,14,17}\) The carboxylic acid group can form interactions with Si surfaces. These interactions yet have not been investigated clearly, but researchers generally accept that they are formed between the hydroxyl groups on the oxidized Si surface and the carboxylic acids of polymer binders. It has been found that the presence as well as the number of terminal carboxylic acid sites (degree of substitution) on the polymer’s monomeric unit affects the cycling performance of Si-based electrode. The higher content of carboxylic groups in the polymer binder should lead to a large number of possible binder-Si bonding points for better cycle performance.\(^{14,17,24,25}\) However, how the hydroxyl groups and carboxylic acid groups react with each other in electrode has not been understood yet.

Hochgatterer et al. showed that CMC was able to chemically bond with Si through a condensation mechanism between the carboxylic groups of CMC and hydroxyl groups on the Si surface during the preparation of electrodes in deionized water at neutral pH.\(^{24}\) The schematic of interaction mechanism is shown in Figure 13.\(^{24}\) This process is described as the
hydroxyl groups and the carboxylic acid groups firstly interact via hydrogen bonding, followed by a condensation reaction with a covalent ester bond established between the polymer and Si. This mechanism can explain the Si-CMC interaction and the improved cycle performance of Si. However, the point that whether the esterification reaction can occur in deionized water at neutral pH value or not is challenged by others. Mazouzi et al. did not observe any esterification reaction when the composite was prepared in deionized water at neutral pH. According to their analysis, they found that the pH 3 buffered condition is mandatory for the esterification reaction to occur between Si and CMC polymer rather than the neutral pH condition (**Figure 14**).

**Figure 13.** Schematic of reaction between hydroxyl groups and carboxylic acid groups.
Figure 14. Study of Si-CMC composite prepared in deionized water and pH 3 buffered solution. (a) pH value as a function of time for Si suspension (full symbols) or CMC solution (open symbols) prepared in DI water (◇, ◆) or a buffered solution at pH 3 (□, ■). The pH value of DI water was also modified by the addition of 10^{-3} M of H2SO4 before the experiment started (○, ●). (b) FTIR spectra recorded in transmission mode of (i) pure nanoparticles of Si, (ii) pure CMC, (iii) Si–CMC composite prepared in DI water, and (iv) Si–CMC composite prepared in buffered solution at pH 3. The XPS spectrum (94–108 eV) in the region of the Si 2p peak of (c) Si–CMC composite prepared in DI water and (d) Si–CMC composite prepared in buffered solution at pH 3.²⁷

Different from the mechanism of ester covalent bond formed between the hydroxyl groups and carboxylic groups, Bridel et al. developed a hydrogen bonding mechanism.²⁸ This hydrogen bonding could enable a self-healing function, which is the breaking and reformation of the bonds to accommodate the volume change of Si and maintain the electrode integrity. Through
modifying the Si surface chemistry by removing hydroxyl groups to stop the formation of ester bond with carboxylic acids of CMC (Si-g1) or adding amino group to facilitate the peptide bond with carboxylic acids of CMC to simulate the formation of ester bond (Si-g2), results show that the absence of Si-polymer interactions and covalent bonding are both detrimental to the electrochemical properties of Si composite (Figure 15). Further investigations by NMR indicates that no Si-O-CO-R ester-like bond between SiO₂ and the carboxylic acid groups of CMC was detected (Figure 16). Without noticing any covalent bonding, authors suggest that the Si-CMC interaction is rooted in a non-covalent bonding mechanism. Although authors could not provide effective evidence to quantitative characterize the bond strength and its dynamics in self-healing behaviour, their work greatly moved forward the study of hydroxyl groups and carboxylic acid groups interaction in Si-binder systems.

Figure 15. Electrochemical performance and schematic of Si-binder interactions.
Extensive studies have been done to study the influence of carboxylic acid groups of CMC on the cycle performance of Si electrode rather than on the individual Si-CMC bonding mechanism. Regarding the electrochemical behavior of electrodes having the two types of bonding, including covalent bonding and hydrogen bonding, it needs to point out that covalent Si-CMC bonding only ensures long-term capacity retention when a limited discharge cut-off voltage is applied. For the hydrogen-type interaction, the low cut-off potential can reach 0 V, allowing the deep lithiation of Si to get the highest capacity. Bridel et al. compared the different two types of bonding electrodes (Figure 17) and elucidated each evolution of Si-CMC bonding as the Li⁺ insertion proceeds (Figure 18). In the schematic model, up to around 1.7 Li/Si, both covalent and hydrogen bonding can sustain the particles volume changes, the
overall swelling being buffered by the electrode porosity. Beyond 1.7 Li/Si, the maximum CMC stretching ability is reached, and only the hydrogen-type Si-CMC interaction allows preservation of the efficient network through a proposed self-healing phenomenon.\textsuperscript{29} Therefore, Si electrode shows a good cycle life with high capacity.

**Figure 17.** Capacity retention for Si/C/CMC (1/1/1 wt) composite electrodes prepared from Si/C suspensions with either natural (NP) or modified (PM) pH. The horizontal dashed line indicates the expected capacity value for full Si lithiation (Li\textsubscript{15}Si\textsubscript{4}).\textsuperscript{29}

**Figure 18.** Schematic model showing the evolution in the CMC-Si bonding as the Li uptake proceeds, from top to bottom.\textsuperscript{29}
Having understood the Si-CMC interactions, researchers turn to seek for new polymer binders with carboxylic acid groups or similar functional groups for Si-based electrode.\textsuperscript{12,14,17,30,31} PAA (polyacrylic acid) polymer for use as a binder in Si-based electrode was first introduced by Yushin’s group.\textsuperscript{14} PAA showed improved binder properties compared to CMC. Due to the similar mechanical properties and functional groups (carboxylic acid groups) of PAA and CMC, researchers suggest that it is the high concentration of carboxylic groups in PAA that form hydrogen bonds with hydroxyl groups on Si surface to obtain good cycle performance of Si-based electrode.

Inspired by the higher concentration of carboxylic groups leads to larger number of bonding points with Si, Yushin’s group introduced alginate, a natural polysaccharide from brown algae, as a binder application for Si electrodes.\textsuperscript{12} Alginate has evenly distributed carboxylic acid groups along the polymer chain while CMC has randomly distributed carboxylic groups with various degree of substitution for each monomeric unit. However, they lack sufficient evidence to support their statement that alginate can provide stronger bonding with Si than CMC can. In their FTIR spectroscopy studies (\textbf{Figure 19}), the decrease of the relative intensity at 1300 cm\textsuperscript{-1}, which is assigned to pyranose ring deformation vibrations, indicates the formation of a chemical interaction between the alginate and Si.\textsuperscript{12} However, no explicit result can be found to support their statement about the chemical interaction between Si and alginate.\textsuperscript{32} For the mechanism of Si-alginate interactions, the authors did not deeply investigate its bonding mechanism; they just used two completely contradictory mechanisms, one is Bridel’s hydrogen
bonding type and the other is Mazouzi’s pH value controlled covalent ester bonding type,\textsuperscript{27,28} to identify the Si-alginate bonding interaction.

\textbf{Figure 19.} FTIR spectra of alginate, Si, and Si electrode with alginate.\textsuperscript{12}

Motivated by mussels with exceptional wet-resistant adhesion properties, Ryou et al. recently developed a novel polymer with rigid polymer backbone (alginate) and adhesive functional groups (catechol) for use as the binder in Si electrodes.\textsuperscript{31} Catechol is the functional group of mussel foot protein 3,4-dihydroxy-L-phenylalanine (DOPA) that contributes to the extraordinarily strong wetness-resistance adhesion.\textsuperscript{31,33–35} The design of mussel-inspired polymer binder is designed by conjugating catechol moieties onto the carboxylic acid functional groups of rigid polymer backbones, such as alginate.\textsuperscript{31} In \textbf{Figure 20a}, the inset shows the chemical structure of dopamine, a commercial chemical, used to provide catechol functional groups. \textbf{Figure 20b} shows the structural formula of catechol conjugated alginate (Alg-C) and catechol conjugated PAA (PAA-C). In the Si electrode, Si particles are strongly adhered with pendent catechol groups on rigid polymer backbones as shown in \textbf{Figure 20c}. 
The single-molecule interaction between polymer binder and Si was studied by AFM technique and results indicate that the Alg-C and Si interaction falls in the force range of covalent bonds (hundreds of pN) while the interaction force of alginate and Si falls in the range of hydrogen bonding (less than 100 pN).\textsuperscript{31,36,37} Therefore, the catecholic interaction is far stronger than the other binding mechanisms of reported polymer binders. This catechol conjugated polymer provides a new principle and binding mechanism for Si electrode and it can be expected that more investigations will be focused on this type of modified polymers as the binder for Si electrodes.

**Figure 20.** Catechol conjugated polymer binder structures and Si electrode.\textsuperscript{31} (a) Mussel; the inset shows the chemical structure of dopamine inspired from mussel foot proteins. (b) Structural formula of Alg-C and PAA-C alongside a simplified structure of a conjugated polymer binder; the black solid line represents the polymer backbone with carboxylic acid functional groups attached and red circles represent catechol moieties conjugated to the backbone. (c) A graphical illustration of the Si nanoparticle anode structure.
Cross-linking of polymer binders

Crosslinks of polymer binders can improve their stiffness and robustness, while reducing the swelling in the electrolyte and maintain the Si-binder strength in electrode. Komaba et al. point out that the linear polymer chains of PAA can be partially bridged by the hydrogen bonding and covalent bonded by the carboxylic anhydride groups between carboxylic acid groups (Figure 21). The cross-linked PAA network could modulate the mechanical and chemical properties against the Si large volume change in the electrode.

Figure 21. ATR-FTIR spectra of the pure polymer films of (a) CMC and (b) PAA.30

Inspired by the cross-linked network of PAA polymers, Koo et al. in Cho’s group developed a three-dimensionally interconnected network of PAA and CMC through condensation reaction to form cross-linked structure.17 The schematic of a crosslinking mechanism is shown Figure 22a-c. The condensation reaction between carboxylic acid groups of PAA and hydroxyl groups of CMC can occur at 150°C under vacuum condition to start the crosslinking.17 Researchers
claimed that the free carboxylic acid of PAA and hydroxyl groups on Si surface could undergo a dehydration reaction to form ester bonds between the binder and Si. There is another possible reaction which the authors neglected that the free carboxylic acid groups from CMC can have the dehydration with hydroxyl groups on Si to form the Si-binder interaction. In the FTIR spectra (Figure 22e), authors attributed the shift of C=O stretching band in COOH of PAA (from 1703 to 1722 cm\(^{-1}\)) to the ester groups (COO) formed by the cross-linking process. They also considered the peak at 1805 cm\(^{-1}\) as the anhydride characteristic bands. It needs to point out that the anhydride mentioned in their work is actually cyclic anhydride. Compared to the Figure 21 and Figure 22, the explanation of peaks in two FTIR spectrum are different.

Figure 22. Schematic of cross-linking mechanism between PAA and CMC and FTIR spectra of polymers.
Building a stable SEI

A stable SEI is important for Si electrode to achieve high coulombic efficiency (CE) and good structural stability. Although results have proved that some binders can help to stabilize the SEI on Si electrode, the question that how polymer binders assist in building the stabilized SEI is still unknown. Due to the complicated SEI formation, it becomes a challenge for researchers to study the evolution of SEI in the binder-assisted Si electrodes.

By comparing the physical and electrochemical properties of binder-assisted electrodes, Komaba et al. believe that it is the uniform polymer coating which reduces the net contact area between the electrolyte and active materials that suppresses the decomposed electrolyte production and continually SEI formation (Figure 23).\textsuperscript{30,38,39} This uniform polymer coating acts as an artificial SEI layer that limits the production of SEI on bare Si surface. However, in our opinion, more evidence is needed to demonstrate that the physical barrier can be considered as an artificial SEI layer in help of building stabilized SEI on electrodes. According to our understanding, artificial SEI should have a controlled ratio of organic and inorganic components to allow good ionic conductivity and meanwhile help reduce the amount of decomposed electrolyte. The polymer binder as a physical barrier is only an electric and ionic insulator, which will provide no benefits to the electrochemical properties of Si and electrolyte. In contrast, it will be hinder the electrons and ions transfer kinetics in charging and discharging process.
Figure 23. Schematic of the proposed mechanism for the SiO power with PAA binders.\textsuperscript{30}

It needs to mention that one important study suggested that interactions between the functional groups of CMC and electrolyte may contribute to the SEI formation.\textsuperscript{40} Ouatani et al. systematically studied the influence of binder (CMC) chemistry on the graphitic anode surface film formation. They observed a stable SEI film and found that CMC exhibited an reactivity towards the electrolyte so that the formed new species consisting a non-negligible part of the surface composition do not disappear upon electrochemical cycling.\textsuperscript{40} These authors attributed the chemical reactivity of CMC to the hydroxyl groups of CMC (mechanism shown below).

\[
\text{LiPF}_6 \leftrightarrow \text{LiF} + \text{PF}_5 \quad (5)
\]

\[
\text{R-OH} + \text{LiPF}_6 \rightarrow \text{R-O-PF}_4 + \text{LiF} + \text{HF} \quad (6)
\]

The PF\textsubscript{4} groups grafted at the surface of CMC binder is an important breakthrough in the understanding of binder and SEI chemistry and it is generally accepted as one explanation for the improved cycling performance of binder-assisted electrodes.
However, some literature gave completely contradictory conclusions about the role of hydroxyl groups affecting SEI films.\textsuperscript{41} Their experimental results indicate that hydroxyl groups react with PF\textsubscript{5} produced from LiPF\textsubscript{6} and the resulting PF\textsubscript{3} groups lead to the decomposition of carbonate solvents, which will lead to fast degradation of Si and increased cell impedance.\textsuperscript{17,41}

Dispute about the mechanism of polymer binders in building stable SEI are ongoing. Although the real mechanism is unclear, experimental results have shown that certain polymers indeed are able to build a stable SEI film on the Si electrode surface.\textsuperscript{12,17} To confirm the point, researchers usually compare the composition of SEI and electrochemical impedance of cells in different charging and discharging cycles. As shown in Figure 24, XPS is applied to survey different elements on cycled Si electrode surface to examine the composition of SEI film. It is found that peaks attributed to the SEI did not discernibly change between 30 and 100 cycles, indicating the formation of stable SEI film on Si.\textsuperscript{17} If SEI film is stabilized on Si by polymer binder, the cell should have constant internal impedance no matter how many cycles it runs. Results of impedance measurements shows that stable interfacial resistance of Si electrode was achieved after 100 cycles as shown in Figure 25, confirming the role of polymer binder in building stable SEI films on Si.\textsuperscript{17}
Figure 24. XPS spectra on Si and binder (cross-linked PAA-CMC) before and after electrochemical cycling.\textsuperscript{17}

Figure 25. Nyquist plot of c-PAA-CMC-assisting Si electrode in different cycles.\textsuperscript{17}
Electrochemical performance of Si-based electrode with different binders

Although different research groups have successfully designed advanced polymer binders for Si, the research improvements in cycling performance need to be considered carefully. In different literatures, the batteries use these new polymer binders show different cycling behaviors.\textsuperscript{12,14,17,31} In Figure 26, polymers, such as CMC, PAA, and PVDF, exhibit different capacities. Therefore, it becomes very difficult for us to select the right polymer binder for the use in high-performance Si electrodes. As a result, it is important and urgent to have a comparative performance study of various polymer binders in Si electrode under the same experimental conditions.

\textbf{Figure 26.} Cycling performance of Si electrode with various polymer binders from four different research groups.\textsuperscript{12,14,17,31}
2.4 Carbon-containing silicon composites for lithium ion batteries

In this section, we will talk about carbon-containing silicon composites as the anode for lithium ion batteries. Composite structures including nanotubes and nanofibers will be reviewed and discussed.

2.4.1 The motivation of carbon coating from carbon-silicon nanoparticles

Electrical conductivity

For batteries, the conductivity of electrode is one of the most important properties. High resistance can lead to rapid decline of the voltage due to the ohmic drop, resulting in poor power capability. In addition, the heat generated according to the ohmic law will increase the temperature within the battery, leading to the degradation of battery life.\(^{42}\) Therefore, minimizing the resistance of the electrode becomes an essential issue in electrode design.

In charge/discharge process, the electrode undergoes the diffusion and conduction of lithium ions and electrons. Active materials have much lower ionic conductivity then the electrolyte and much lower electrical conductivity than carbon black additives. Therefore, as shown in Table 1, the resistance of the electrode mainly comes from (a) the electronic and ionic resistance of active particles and (b) the interfacial resistances from electrolyte/electrode interface and particle/particle boundaries.\(^{42}\) To ensure sufficient electrical and ionic conductivity of active particles, carbon coating is needed to supply fast electrons and allow permeation of lithium ions from the surrounding electrolyte. In Figure 27, different conduction/diffusion behavior of electrons and lithium ions is illustrated. With the help of a
carbon coating, effective ambipolar (electronic and ionic) diffusion of electrons and ions get into/out of active particles regardless of particle conductivity. If the electrical conductivity is much lower than the ionic conductivity, the ambipolar diffusion can only occur at the vicinity of contact point, leading to a constrained electric field around this area. If the electrical conductivity is much higher than the ionic, the electrons will disperse around the surface to form double layer of electrons and ions, causing ambipolar diffusion into/out of bulk particles.

Table 1 Internal resistance of an electrode.

<table>
<thead>
<tr>
<th>Resistance type</th>
<th>Internal resistance of a cell ( R = R_1 + R_e + R_{in} )</th>
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<tr>
<td>Ionic ( (R_i) )</td>
<td>Electrode active particle</td>
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<td>Electrical ( (R_e) )</td>
<td>Electrode active particle</td>
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<td>Interfacial ( (R_{in}) )</td>
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<td>Between electrode active particles</td>
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<td>Between electrode particles and conductive additives</td>
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<td>Between conductive and additives and current collector</td>
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</tbody>
</table>
Figure 27. Schematic conduction/diffusion of electrons and lithium ions within a single active particle. (a) Perfect carbon coating around active particles. Electrons are homogeneously distributed around the active particle. Ions are supplied uniformly from the surrounding electrolyte. (b) Point-contacting by a small carbon black particle. Electronic conductivity is assumed to be much lower than ionic. (c) Same as (b) except that that electronic conductivity is much higher than ionic.\textsuperscript{43}

Although nano-sized active particles have short lithium ion diffusion distance, which can help increase the rate capability of batteries, the fact that nanoparticle tends to agglomerate because of high surface energy makes nanoparticles difficult to disperse and mix with conductive additives for a higher energy density.\textsuperscript{42,45} In addition, only small amount of nanoparticles in the agglomerates can contact with carbon, which increases the electron transport distance and increases the interfacial resistance.\textsuperscript{42,45} As indicated in Figure 28, the electron transport length can be shortened by applying carbon coating onto active particles. Continuous electron path is
formed along the particle surfaces, which can greatly reduce the interfacial resistance between particles.

**Figure 28.** Schematic representation of the electron transport length in a nanoparticle based electrode: (a) without carbon coating; (b) with carbon coating.⁴²,⁴⁵
Chemical and electrochemical stability

Carbon exhibits a wide electrochemical stability window in organic electrolytes. Carbon’s electrochemical activity only occurs at very low potential and it will not be oxidized at high cut-off voltages. In addition, carbon has a good chemical stability to organic electrolytes and side-products of the electrolytes. Furthermore, carbon can help prevent active material contacting with oxygen and moisture so as to avoid the degradation of materials in air (Figure 29). Therefore, the carbon coating will not only slow down the degradation of active materials during storage but also enhance the cycling performance.42

Figure 29. Schematic illustration showing the long-term degradation of active materials in air and in electrolyte without (a) and with (b) the carbon coating.42
Physical properties

Carbon exhibits many unique physical properties, such as anisotropic conductivity, low density, high mechanical strength, and structural flexibility, which are very important to be used as coating material in electrodes. Carbon coating in the form of a thin film layer can be uniformly coated on the surface of active material by chemical vapor deposition (CVD) or in situ pyrolysis of carbon precursors. The adhesion of carbon on active material surface is due to the fact that the carbon chooses the structure of deposit in the form of amorphous carbon with a small hardness (10GPa), which allows the carbon coating to adjust the surface roughness and the curvature of the active particles compared to the metal oxide coating method. A layer-by-layer assembly of hexagonal atom planes in the form of sp² bonding provides excellent electrical conductivity and the micro-pores of the coating layer can facilitate the ion transport to the inner active particles. In addition, the carbon coating can also help accommodate the volume changes of active material during lithiation/delithiation process and prevent the active material from separating from the electrode.

Figure 30. Schematic illustration showing different adaptability of the carbon coating and the metal oxide coating.
2.5. Carbon nanotube-based Si nanostructures for lithium-ion batteries

Carbon nanotubes (CNTs), as an important allotrope of carbon, exhibit unique properties including high electrical conductivity, high surface area, good mechanical properties, and stable electrochemical properties, and hence they can act as promising electrode materials in energy and storage systems.\textsuperscript{47–52}

In the electrode design, CNTs have been widely used as the conducting additive in slurry paste by forming an electrical percolation network. Compared to carbon black, CNTs increase the number of electrical contact points of active nanoparticles so as to enhance the rate capability of the electrode. A CNT network can also provide additional mechanical strength to prevent the crack and pulverization of the electrode structure during the structure changes (Figure 31).\textsuperscript{52}

![Figure 31. Schematic of a traditional Si anode composed of carbon-coated Si nanoparticles and binder.\textsuperscript{52}](image-url)
Since CNTs have the capability to store lithium ions, CNTs as alternative anode material have been widely studied as a replacement for graphite in lithium-ion. Work has been done to synthesize CNTs structure and morphologies to make improvement in lithium storage capability. With only a small improvement in capacity compared to the capacity of graphite (375 mAh/g), the difficulties to synthesize CNTs make pure CNTs impossible to apply to the high energy density lithium ion batteries.

Due to the large surface area, porous structure, light weight, flexibility and applicable surface functionality, CNTs can serve as an ideal substrate to support active materials for the higher energy density requirement. Furthermore, different forms of CNT-based electrode can be tailored, such as binder-free electrode with CNTs directly grown on the current collector, and flexible electrode with no polymer binder and current collector in it. Therefore, introducing high capacity active material, silicon, to the various forms of CNTs matrix becomes an effective and promising way to maximize the utilization of both silicon and CNTs in the high energy density electrode design.
2.5.1 Structure, synthesis and properties of CNTs and the mechanism of lithium ion storage

CNTs are 1D material with a high length-to-diameter ratio (>1000). A CNT can be envisioned as a cylinder composed of one or several graphene sheets around a central hollow core with the diameter on a nanoscale and end caps with a hemisphere of fullerene structure.\(^\text{48}\) There are two types of CNTs: one is single-walled carbon nanotubes (SWCNTs) consisting of a single graphene layer and the other is multi-walled carbon nanotubes (MWCNTs) consisting of two or more graphene layers with van der Waals forces in between.

Primarily, there are four methods to synthesize CNTs: arc-discharge,\(^\text{53,54}\) laser ablation,\(^\text{55}\) gas-phase catalytic growth from carbon monoxide,\(^\text{56}\) and chemical vapor deposition (CVD) from hydrocarbon.\(^\text{57}\) Among these four methods, CVD provides a potential for the production of large quantities of CNT at a low cost.\(^\text{48}\)

According to the different rolling angle of the graphene sheet against the tube axis, CNT is described in terms of the tube chirality, which is defined by the chiral vector, \(C_h=na_1+ma_2\), and the chiral angle, \(\theta\) (Figure 32).\(^\text{58}\) By using this naming scheme, there are three types of chirality in CNTs: “armchair” with \(n=m\), “zigzag” with \(m=0\), and the others are called “chiral” (Figure 33).\(^\text{58}\) The chirality of CNTs has significant implication on their electrical properties, such as electrical property. Whether a CNT is metallic or semiconducting depending on the tube chirality.\(^\text{58}\) For MWCNTs, multiple layers of graphene exhibit different chirality, and
hence it is complicated to predict the electrical conductivity of MWCNTs compared to SMCNTs.

Figure 32. Schematic diagram showing how a hexagonal sheet of graphite is rolled to form a carbon nanotube.\textsuperscript{58}

Figure 33. Illustrations of the atomic structure of armchair and zig-zag nanotube.\textsuperscript{58}
Thanks to the strong chemical bonding of sp$^2$ carbon-carbon bond in the perfectly structured CNTs, they have extraordinary physical properties (Table 2), which allows CNTs as an ideal material for use in lots of fields, especially in energy storage application.

**Table 2 Physical properties of carbon materials.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Graphite</th>
<th>Diamond</th>
<th>C$_{am}$</th>
<th>SWCNT</th>
<th>MWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity (g/cm$^3$)</td>
<td>2.05-2.23</td>
<td>3.5</td>
<td>1.7</td>
<td>0.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Electrical conductivity (S cm$^{-1}$)</td>
<td>2.5 x $10^5$</td>
<td>10$^{-9}$</td>
<td>10$^{-8}$</td>
<td>10$^{-10}$</td>
<td>10$^{-10}$</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>3.3'</td>
<td>300-2200</td>
<td>0.4</td>
<td>~6000</td>
<td>~2000</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (K$^{-1}$)</td>
<td>$-1 \times 10^{-5}$</td>
<td>$1-3 \times 10^{-6}$</td>
<td>$62 \times 10^{-5}$</td>
<td>Negligible</td>
<td>Negligible</td>
</tr>
<tr>
<td>Thermal stability in air (℃)</td>
<td>20-100</td>
<td>777</td>
<td>&gt;600</td>
<td>&gt;600</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Surface area (m$^2$ g$^{-1}$)</td>
<td>Variable</td>
<td>10-50</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>30-350</td>
<td>500-1000</td>
<td>14</td>
<td>1200</td>
<td>1000</td>
</tr>
</tbody>
</table>

* p: in-plane and c: c-axis.

Before addressing the mechanism of lithium ion storage in CNTs, we have to understand lithiation behavior in graphite material. Graphite is the commercialized anode material in lithium ion batteries. Graphite is characterized as a stack of hexagonal-bonded carbon sheets with van der Waals forces holding the sheets together. The forces between any two carbons in the same sheet, which share sp$^2$ hybridized bonds, are much stronger than the forces between any two concurrent sheets. It is the difference of force that enable lithium ions to insert into the interspace between planes, which is termed as insertion or intercalation. When one lithium ion occupies an interstitial site between two planes, and this keeps more lithium ions from binding in the adjacent interstitial sites, and limits the amount of lithium ions to 1 for every 6 carbon atoms as LiC$_6$. This is directly related to the energy density of graphite (Figure 34).
CNTs exhibit a different intercalation mechanism for lithium ions. For CNTs, the capability of lithium ion storage is largely depending on their morphologies, particularly the defects on the wall.\textsuperscript{47} The defects can occur naturally or can be introduced by acid treatment. It is found that the defects in the forms of holes on the wall allow fast lithium ion diffusion and lithium ions intercalation into the internal space of CNT.\textsuperscript{59–61} As shown in Figure 35, lithium ions are able to diffuse into CNTs with \( n = 9 \) defect, where \( n \) means the number of carbon ring defect. Once the lithium ions diffuse into the CNTs, they can move though the tube interior.\textsuperscript{62} However, the introduction of defects will also increase the irreversible capacity, which means that once lithium ions are inserted, they cannot exit if the tube is too long.\textsuperscript{63} A related problem of CNT anodes is the lack of a voltage plateau during discharging (Figure 36), making CNT anodes difficult to use in most electronics which requires a stable voltage range.\textsuperscript{47}
Figure 35. Effect of defects on lithium ion insertion in (5,5) SWCNTs.\textsuperscript{62}

Figure 36. A schematic representing typical discharge curves of a graphite and CNT anode, respectively.\textsuperscript{47}
Fundamental studies on the mechanism of lithium storage in CNT has been discussed for a long time, however, no significant improvement in the CNT capacity has been achieved. The capacity was usually lower than 600 mAh/g and some even much lower than 375 mAh/g (of graphite), which is far from the requirement of higher energy density electrode for electric vehicle. The limited understanding of the synthesis of CNT make it difficult to control the morphology of single CNTs as well as the structure of CNT forests, hindering the possibility of CNT applied by themselves in energy storage applications.

In order to achieve the goal of high energy density, researchers are turning into applying active materials with high theoretical capacities to the CNT matrix, by using CNTs’ superior physical properties, such as electrical conductivity, low density, and large surface area, rather than lithium ion storage capability.

2.5.2 Carbon nanotube-Si electrode design for lithium ion batteries

Before discussing CNT-Si electrodes, it is necessary to understand the configuration of lithium-ion batteries and introduce related concepts, such as binder-free and flexible batteries.

Routes for designing high-energy lithium-ion batteries

For high-energy lithium-ion batteries, the first important component is to have high energy electrodes. Active materials with high capacity and efficient binder systems play the essential role in achieving the high energy density of electrodes (Figure 37). The preparation of a conventional electrode is based on the slurry-casting method, having the active materials mixed with polymer binder and conducting additive. The fresh mixture is then pasted onto a copper
(negative electrode) foil and dried to obtain a piece of electrode. The role of binder system has been well reviewed and discussed earlier this chapter. However, due to the intrinsic properties of binder system (conducting additive and polymer binder), it is inevitable to decrease the electrical conductivity of active materials and meanwhile bring side effects between inactive materials and the electrolyte even if the composition of the electrode is well controlled. Consequently, the cycling performance will be detrimentally affected and the overall gravimetric energy density of the electrode will be reduced by the inactive binder system. Therefore, eliminating the conducting additive and polymer binder is the first step to design high-energy electrodes.

![Figure 37. Schematic of (a) conventional and (b) flexible electrode components in lithium-ion batteries.](image)

An electrode without the presence of conducting additive and polymer binder can have simplified electrode preparation process and exhibit greatly improved cycling performance as well as high energy density. This one can be categorized as binder-free electrode. Normally, such binder-free electrodes still keep the current collector, e.g., copper foil for the negative
electrode, providing the structural support and electron pathway to active material. It needs to mention that the active material composite often has an electrical conductive coating, e.g., carbon layer, so that sufficient electron transport pathway can be bridged from the current collector to active materials.

However, to further increase the energy density of the overall electrode, the metal current collector must be removed in order to reduce the total electrode weight. The copper current collector account for 10-15% of the total weight of a cell with a copper areal density of 13.0 mg/cm$^2$. Therefore, free-standing electrodes, having no conducting additives, polymer binders or current collectors, give the second step to achieve higher energy density. Therefore, we can follow the route as shown in Figure 38, to design a high energy density electrode by eliminating the inactive materials.

**Figure 38.** Route of design a high-energy electrodes.
**Conventional CNT-Si electrode**

As far as we know, the CNT-Si design was first reported from Kumta’s group in 2010. It was the first time to present a template-free design and fabricate a core-shell structure of CNT-Si electrodes. This core-shell structure enables the CNT core to provide mechanical strength and conductivity and the silicon shell in the form of nanoclusters or layer coatings to deliver high capacity, as shown in Figure 39.

![Figure 39. Schematic of CNT-Si nanostructure.](image)

In their work, MWCNT forest was first synthesized on a quartz slide in a CVD system by using liquid injection of xylene (C₆H₁₀) as the hydrocarbon source and ferocene (Fe(C₅H₅)₂) as the catalyst, and then silicon was deposited by the decomposition of silane (SiH₄) gas. The morphology of CNT-Si is shown in Figure 40. It can be observed that silicon nanoclusters are uniformly coated on CNTs and meanwhile CNT forests remain intact after silicon deposition.
**Figure 40.** Morphology of CNT-Si nanostructure. (a) SEM image of the aligned pristine carbon nanotubes prior to silicon deposition. (b) A low-magnification SEM image showing multiple clusters of carbon nanotubes covered with silicon nanoclusters. (c) TEM image of a single carbon nanotube covered with multiple silicon nanoclusters with spacing in between each other. (d) HR-TEM image showing different directions of the lattice fringes within a single silicon nanoparticle (white lines indicate the different lattice orientations).  

The as-prepared CNT-Si forests were scraped off from the quartz slide and mixed with polymer binder and conducting additive to prepare the electrode for electrochemical evaluation. The electrochemical properties are shown in **Figure 41.** The good electrochemical performance of CNT-Si is attributed to the core-shell structure and silicon nanoclusters coating, which help relax the strain of silicon during volume change and ensure short electron pathway from CNT to silicon. However, only around 20 cycles of charge and discharge process are given.
Figure 41. Electrochemical properties of conventional CNT-Si electrode. (a) Voltage profiles for hybrid CNT-Si nanostructures anode after 1, 10, and 25 cycles. (b) Curve of discharge/charge capacity and Coulombic efficiency of the cell over 25 cycles. (c, d) Plots of differential capacity with cell potential of hybrid CNT-Si nanostructures anode: (c) after 1st and 2nd cycle, (d) after 2nd, 10th, and 25th cycle. 

It needs to mention that the composition of the mixture is 50 wt.%, 10 wt.%, and 40 wt.% of CNT-Si, carbon black, and binder, respectively. The low active material loading and high inactive material content induce high electrical resistance and many side reactions, which are detrimental to the cycling performance of the electrode. In addition, the overall energy density of the electrode was compromised by the large content of inactive materials. These problems can partially explain limited of cycling performance for their CNT-Si electrode.
Binder-free CNT-Si electrode

Inspired by the idea of core-shell CNT-Si nanostructure, binder-free CNT-Si electrodes were designed and fabricated. In this approach, every CNT is grown directly onto the current collector to achieve direct electron transport, so that binder and conducting additive are no longer needed, which simplifies the electrode preparation process and ensures good electrochemical performance of active materials. This binder-free CNT-Si electrode is also termed as vertically aligned CNT-Si electrode.

The earlier work of vertically-aligned CNT-Si electrodes was first-reported from Kumta’s group in 2011. The schematic diagram of their preparation process is shown in Figure 42. Inconel alloy disk, which is a nickel-chromium alloy, is used as the substrate to grown CNTs directly on its surface, followed by depositing silicon on the CNTs surface. The as-prepared vertically aligned CNT-Si with Inconel disk as the current collector serves as an integral electrode for lithium ion batteries.

Figure 42. Schematic of vertically aligned CNT-Si electrode.
The morphology of their vertically aligned CNT-Si electrode is shown in Figure 43. Vertically aligned CNT-Si arrays can be seen grown on the substrate and large silicon nanoclusters are coated on the surface. By controlling the silicon deposition time, different silicon nanocluster structures are created. Figure 43 c-d show a single CNT covered with multiple silicon nanoclusters at defined spacing for the shorted deposition time, and the one covered with continuous silicon layer for a longer deposition, respectively.

Figure 43. Morphology of vertically aligned CNT-Si electrode. (a) SEM image of MWNTs on Inconel disk. Insert image showing the HR-TEM image of a nanotube. (b) SEM image of the MWNTs on Inconel disk after silicon deposition (c) and (d) HR-TEM images of a single carbon nanotube covered with multiple silicon nanoclusters at defined spacing, and with continuous coatings of silicon layer after different deposition times.

The electrochemical properties of the vertically aligned CNT-Si electrode is give in Figure 44. Compared to the result of their previous work, the cycling performance is slightly
worse. They did not explain the reason, but according to the SEM images of vertically aligned CNT and CNT-Si, we assume that it has possibility according to the poor electrical connection between the CNT-Si and the Inconel substrate. In addition, silicon coating on the empty space between the gaps of CNT-Si and the substrate may block the electron transport, which directly leads to the poor cycling stability.

Figure 44. Electrochemical properties of vertically aligned CNT-Si electrode. (a) Voltage profiles for hybrid silicon/CNT nanostructures anode after 1, 10 and 30 cycles. (b) Curves of discharge/charge capacity and Coulombic efficiency of the cell over 30 cycles. (c) and (d) Plots of differential capacity with cell potential. 

Realizing the high capacity of core-shell CNT-Si structure (>2000 mAh/g), researchers started the systematic study of the core-shell design for CNT-Si and in situ observations are made to give a better understanding of the core-shell structure of CNT-Si. According to their study, CNTs with large diameters would be advantageous because of their reduced curvature effect and large inter-tube space between nanotubes would be good to accommodate the volume
change of silicon and allow the electrolyte access.\textsuperscript{70} Therefore, the morphology of both CNT core and silicon shell need to be rationally tailored to make good use of free space and optimize the advantage of this core-shell structure as electrodes for lithium-ion batteries.\textsuperscript{70}

Rationally designed core-shell CNT-Si electrodes have been reported from Zhang’s group at Nanyang Technological University.\textsuperscript{70,71} A schematic image of their CNT-Si electrodes is shown in Figure 45. The vertically aligned core-shell CNT-Si forest with large inter-tube space can be beneficial to both the silicon volume change and the electrolyte diffusion. The CNT forest was synthesized by using nickel as the catalyst, which is deposited onto a stainless steel (SS) before CNT grown, in a plasma enhanced CVD (PECVD) system.\textsuperscript{70} The diameter and inter-tube space of individual CNT can be controlled by the thickness of the nickel catalyst film.\textsuperscript{70} The silicon coating was applied by RF magnetron sputtering system.\textsuperscript{70}

\textbf{Figure 45.} Schematic of fabrication process and structure of rationally designed CNT-Si.\textsuperscript{70} The morphology of CNT-Si is given in Figure 46,\textsuperscript{70} which shows a uniform CNT forest with good vertical alignment and sufficient free space between each CNT. After silicon coating,
large inter-space is still maintained. It is noticed that the silicon coating exhibits a gradient morphology with its thickness gradually decreasing from the top to the root of the CNT, forming a cone shaped silicon coating. This cone shaped silicon coating is formed due to the un-uniform deposition of sputtered silicon. It makes sense that top region of CNT would see a higher silicon deposition than the CNT roots.

![Figure 46. Morphology of rationally designed CNT-Si. (a) Tilted angle SEM image of the CNT arrays, (b) tilted angle and (c) top view SEM images of the CNTs with cone shaped silicon coatings, (d) TEM image of a single CNT–silicon nanowire.](image)

This rational design leads to a superior cycling performance, as shown in Figure 47. Note that the capacity is based on the mass of silicon instead of CNT-Si. Although the capacity can be compromised when the mass of CNT is considered, this rationally designed CNT-Si
electrode exhibits a significantly improved cycling stability, with 90.4% retention of the initial capacity after 100 cycles.

![Graph showing electrochemical properties of rationally designed CNT-Si electrode.](image)

**Figure 47.** Electrochemical properties of rationally designed CNT-Si electrode. (a) Lithiation/de-lithiation capacities and Coulombic efficiency versus cycle number at 0.2 C, (b) the voltage profiles of the CNT–silicon anode in the 100th cycle.70

The above-mentioned rationally designed CNT-Si electrode demonstrates the possibility of maximizing the silicon in the core-shell structure. However, this type of binder-free design has one shortcoming, the metal current collector. The presence of metal current collector will greatly decrease the gravimetric energy density of the overall electrode. In addition, the limited length of CNT forest with large inter-tube space will also reduce its volumetric energy density. Therefore, to greatly improve the energy density of the CNT-Si electrode, two strategies are developed: one is to substitute the metal current collector by other electrical conducting substrate; and another is to remove the metal current collector.
To find a lightweight and electrical conducting substrate is very important for the improvement of overall electrode energy density. Graphene is an ideal substrate. If the above-mentioned CNT-Si forest can grow onto a graphene layer, the overall energy density will be largely improved. But till now, as far as I know, no publication has ever been reported on such idea for lithium-ion batteries. In future research, we can conduct the synthesis of graphene-based CNT growth and I believe that this design having graphene as the substrate with vertically-aligned CNT grown on it can potentially solve the current problems in electrode design.

The other way to increase the overall energy density is to remove the metal current collector. Without the support of current collector, active materials must still keep the self-supported structure and good electrical conductivity to ensure the formation of electrode and achievement of electrochemical properties. Self-supported, flexible CNT assemblies provide many possibilities to achieve our goal of high energy density.

*Self-supported CNT-Si electrode*

Due to low density, high surface area, high mechanical conductivity and mechanical flexibility, CNTs can be easily assembled into self-supported membrane or paper-like structure, exhibiting light weight, good flexibility and mechanical stability. Most reported CNT-Si structures are focused on the CNT nonwoven structure, which contains self-entangled CNT with random orientation.\(^{68,72−74}\) Recently, new structures have been developed, such as twisted CNT-Si yarns and weaveable woven structures, which bring novel architectures to the versatile battery design.\(^ {75,76}\)
Light-weight free-standing CNT-Si film structure was first reported from Cui’s group at Stanford University in 2010. Cui’s group first introduced the light-weight and highly conductive CNT network as both a mechanical support and an embedded-in current collector. The schematic design is shown in Figure 48.

![Schematic design of CNT-Si film comparison](image)

**Figure 48.** Schematic of flexible CNT-Si films compared to the sputtered-on Si film. (a) Sputtered-on Si film tends to pulverize after Li⁺ cycling. (b) CNT-Si films can “ripple up” to relax the large strain during Li⁺ cycling.

The CNT film is assembled by drying method, i.e., removing the solvent from the CNT dispersed solution to get intertwined CNTs. Silicon was deposited onto the CNT film using the CVD process. The structure of CNT-Si film and its electrochemical properties are show in Figure 49. High capacity was shown but still it gives decreasing trend in the long cycles.
Figure 49. Flexible CNT-Si film and its electrochemical properties. (a) Photograph of a free-standing CNT-Si film. (b,c) Charge (red) and discharge (green) capacity and Coulombic efficiency (blue) versus cycle number for a half cell using free-standing CNT-Si films as the working electrode cycled between 1–0.01 V, where (b) uses a single-layer, free-standing film and (c) uses two layers of free-standing films. (d) Voltage profile of the cell in (b).\textsuperscript{72}

Similar work was produced by several other groups during the same period of time. SWCNT-Si paper as a battery was reported by Wang’s group at University of Wollongong in 2010 (Figure 50).\textsuperscript{73} SWCNT paper was prepared by filtration method to form a self-supported CNT network. Silicon was deposited onto/into SWCNT paper by using pulsed laser deposition (PLD) technique. However, due to the small silicon content (<11.0 wt.%), the overall electrode capacity cannot meet the demand of high energy density (Figure 51).\textsuperscript{73}
**Figure 50.** Morphology of SWCNT-Si paper as electrode for lithium ion batteries. Typical low (a, b) and high (c) magnification SEM images of Si/SWCNT composite paper obtained from PLD with 30 min deposition time, with top (a, c) and cross-sectional (b) views. EDX spectrum (d) taken from (a). Inset of (d) is a photograph of the Si/SWCNT composite paper. The scale bar in (a), (b), and (c) is 5, 1, and 0.5 μm, respectively.\(^7\)

**Figure 51.** Cycling performance of SWCNT-Si paper electrode. (a) Cycle life and (b) capacity retention of pristine SWCNT paper and Si/SWCNT composite paper electrode with silicon contents of 2.2% and 11.0% at a current density of 25 mA/g. The cycles are all between 0.01 and 2.0 V vs Li/Li\(^+\) at 25 °C.\(^7\)
Cui’s group reported CNT-Si sponge structure, exhibiting good volume retention, highly porous and conductive structures (Figure 52). From the SEM and TEM images, uniform silicon coating is formed along the CNT surface, which is mainly due to the highly porous nature and large inter-tube space of the structure. By controlling the cut-off voltage, CNT-Si sponge gave a high capacity with stable cycling life in 50 cycles (Figure 53).

**Figure 52.** Morphology of porous CNT-Si sponge. (a) SEM image of a 3D porous CNT sponge. The CNTs are entangled and form a highly conductive network. The inset shows a picture of a CNT sponge 1 cm × 1 cm × 8 mm in size. (b) SEM image of 3D porous Si–CNT sponge. (c) Close-up view of (b) showing the coaxial structure of amorphous Si conformally coated around CNTs. (d) TEM image of a coaxial Si-CNT structure showing the thickness of the Si coating is approximately 30 nm. The inset shows the TEM diffraction pattern of this coaxial Si–CNT structure.
Figure 53. Electrochemical properties of CNT-Si sponges as electrode for lithium ion batteries. (a) Voltage profile of a Si–CNT coaxial shell–core structure with Li metal as the counter electrode at a charge rate of C/5 and with an operation voltage range of 0.05–1.00 V. The numbers 1, 2, 10, 20 and 40 indicate different cycles. (b) Voltage profile of a Si–CNT coaxial structure vs Li metal counter electrode at a rate of C/5 and an operation range of 0.17–1.0 V. (c) Cycling performance of Si–CNT coaxial structures at different voltage ranges.68

Although the above-mentioned self-supported CNT-Si structure exhibits good cycling performance, the poor mechanical strength limits the continuous fabrication of CNT matrix and makes the large-scale application impossible. Therefore, to design a CNT structure with high tensile strength becomes important and practical. In 2012, an ultra-strong CNT-Si nonwoven fabric as the battery electrode was developed by Yushin’s group at Georgia Institute of Technology.74 CNT was produced by using floating ferrocene as the catalyst and sulfur as the conditioner in a CVD system with ethanol as the carbon source. Upon exiting the furnace
hot zone, the CNTs were collected onto a moving belt or drum until the required dimensions are obtained. They mentioned that CNTs could be extracted from the furnace and underwent certain treatment to enhance their electrical and/or mechanical properties. But they did not provide any details about how to collect the CNT into a nonwoven fabric and how the treatment was conducted to the as-made CNT fabric. CVD silicon deposition is applied to the as-made ultra-strong CNT fabric. The structure is shown in Figure 54. This CNT-Si nonwoven fabric shows a superior mechanical strength compared to other common materials (Figure 55). The electrochemical properties are shown in Figure 56. Although its capacity had only around 500 mAh/g, the superior stable cycling performance was much better than others’ work.

![Figure 54. Morphology of ultra-strong CNT-Si nonwoven fabric. (a,b) SEM micrographs and (c,d) photographs of the CNT fabric (a,c) before and (b,d) after Si coating.](image)
Figure 55. Mechanical characterization of the ultra-strong CNT-Si nonwoven fabric. (a) typical tensile tests on CNT fabric before and after annealing in Ar; (b) typical tensile tests on Si-coated CNT fabric before and after cycling; (c) comparison of the specific strength of the multifunctional Si-coated CNT fabric with that of other common materials.\textsuperscript{74}
Figure 56. Electrochemical properties of ultra-strong CNT-Si nonwoven fabric as electrode. 
(a) reversible de-alloying (Li extraction) capacity versus cycle number in comparison to the synthesized CNT fabric; (b) changes in the charge and discharge profiles with cycle number; (c) cyclic voltammograms.\textsuperscript{74}

In addition to the random-oriented CNT-Si structures, the twisted CNT-Si yarn and CNT-Si woven textile fabric have also been reported as electrodes for lithium-ion batteries.\textsuperscript{75,76} The CNT-Si structures in the form of yarns or woven fabrics were assembled from the spinnable CNT arrays, which were synthesized in CVD system. The concept of spinnable continuous carbon nanotube yarns was first introduced by Fan’s group at Tsinghua University in 2002.\textsuperscript{77} It needs to mention that though it is relatively easy to synthesize a CNT forest, not all CNT forests are spinnable. The condition to synthesize spinnable CNT forests is so narrow that only
a handful of groups are able to produce CNT yarns out of CNT forest even 10 years after the first introduction of this technique.\textsuperscript{78}

Peng’s group at Fudan University reported the successfully synthesis of a twisted aligned CNT-Si composite yarn as the electrode for lithium-ion batteries in 2013.\textsuperscript{76} The schematic image of the yarn preparation is shown in Figure 57.\textsuperscript{76} Aligned CNT sheet was firstly drawn out of the spinnable arrays and then silicon was deposited onto the sheet through atomic layer deposition followed by a twisting treatment to form a flexible composite yarn, which can be used as an electrode directly.\textsuperscript{76}

\textbf{Figure 57.} Schematic image of the preparation of the aligned CNT-Si yarn.\textsuperscript{76}

The morphology and composition characterizations are given in Figure 58.\textsuperscript{76} After silicon coating, CNTs were maintained as highly aligned, and no obvious aggregates are observed in the composite. The Raman shift of silicon peak indicates the poor crystallinity of silicon formed on the CNT surface. According to the above-mentioned work, it seems that only CVD
method can build high crystalline silicon, which is good for the electrochemical performance of CNT-Si electrode.

Figure 58. Morphology and composition characterizations of the aligned CNT-Si yarn. (a,b) SEM images of a bare aligned MWCNT fiber at low and high magnifications, respectively. (c,d) SEM images of an aligned MWCNT/Si composite fiber with Si weight percentage of 38.1% at low and high magnifications, respectively. (e) X-ray diffraction pattern of the MWCNT/Si composite. (f) EDX analysis of the aligned MWCNT/Si composite fiber (insert: HR-TEM image of an aligned MWCNT/Si composite fiber with a Si weight percentage of 38.1%).

The electrochemical performance is give in Figure 59. Quickly decreasing capacity is observed in the first 50 cycles, which is possibly due to the unconstrained CNT-Si yarn structure during the significant silicon volume change and the electrical conductivity issue of
the closely twisted CNT-Si. The fast capacity fading makes the further optimization of this aligned CNT-Si yarn necessary to improve the cycling stability in the long run.

Figure 59. Electrochemical performance of aligned CNT-Si yarn. (a) Typical charge and discharge curves of a half lithium-ion battery based on the bare aligned MWCNT and aligned MWCNT/Si composite fibers with a Si weight percentage of 38.1% at 1 A/g. (b) Specific capacities of the wire-shaped bare and composite fibers with different Si weight percentages at 1 A/g. (c) Dependence of the specific capacity on current density. (d) Dependence of the specific capacity on cycle number.\textsuperscript{76}

Wang’s group at University of Maryland reported the textile design of woven CNT-Si fabric as the electrode for lithium-ion batteries in 2013.\textsuperscript{75} CNTs were firstly spun into a yarn from spinnable CNT arrays grown in CVD system. Then the CNT yarn was treated by CVD silicon
coating. Finally, the CNT-Si yarn was fabricated into a woven textile fabric. The schematic and morphology characterization are shown in Figure 60 and Figure 61.

**Figure 60.** Schematic of the fabrication of the weavable CNT-Si fabric. (a) Drawing a CNT thin film from a vertically aligned CNT array. (b) CNT yarn spun by a two-fold spinning process. (c) Silicon-coated CNT yarn. (d) Textile wove from composite yarns.
**Figure 61.** Morphology characterization of the weavable CNT-Si fabric. (a) Optical image of a CNT thin film drawn from vertically aligned a CNT arrays. (b) SEM image of CNT yarn. ((c)–(f)) SEM images of CNT-Si composite yarns. (d) The composite yarn is wrapped round a copper rod, showing a high level of flexibility and durability. (e) SEM image of a textile woven from CNT-Si yarns. ((f) and (g)) The porous structure of the CNT-Si composite yarn. (h) TEM images resolving the CNT-core, Si-coating and CNT-Si interface. Inset is a high resolution TEM image that clearly shows the CNT-Si interface.\(^{75}\)

Although the weavable textile of CNT-Si fabric is well-designed, the fast capacity decay is still the challenging issue as shown in **Figure 62.**\(^ {75}\) Therefore, to find effective way of maintaining the cycling stability of self-supported electrodes are what we will do in my Ph.D. studies.
2.6 Carbon nanofiber-based Si nanostructure for lithium-ion batteries

2.6.1 Carbon nanofibers (CNFs) as the anode for lithium-ion batteries

Carbon nanofibers directly used as the anode for lithium-ion batteries were first introduced by Kim’s group at Shinshu University in 2005. By a combination of electrospinning and thermal treatment, electrospinning-derived carbon nanofiber webs were fabricated with good mechanical and electrochemical properties, exhibiting as a potential candidate for use as an anode material in lithium ion batteries.
In their work, polyacrylonitrile (PAN) was used as the carbon precursor to be electrospun into PAN nanofiber. Undergoing the stabilization and carbonization process, carbon nanofibers was obtained. The stabilization temperature was fixed at 280°C, which is based on Jiang’s work at China Textile University (now Donghua University) in 1986. The structure property and the electrochemical property of carbon nanofibers prepared at different temperature, from 700 to 2800 °C, were shown in Figure 63 and Figure 64. It should be mentioned that carbon nanofiber mats were electrochemically evaluated directly as the electrode without any binder or conducting additives. According to their results, the low-temperature treated carbon nanofibers (700 and 1000°C) are suitable for stable lithium ion batteries due to their constant and slightly inclined charge potential.

![Figure 63. Raman and XRD characterization of carbon nanofibers.](image)

Figure 63. Raman and XRD characterization of carbon nanofibers.
Inspired by this study, a porous carbon nanofiber electrode was designed in Zhang’s group at North Carolina State University. The porous carbon nanofiber structure was believed to provide numerous active sites for charge transfer reaction, short diffusion pathway for both lithium ions and electrons and good electrical conductivity. Polylactic acid (PLA) was used as sacrificial component for the pore formation. Under the thermal treatment, PLA would be decomposed and PAN turned into carbon nanofibers with the pores left by PLA, as shown in Figure 65. Thanks to the porous structure, the specific surface area increased from 33.9 m$^2$/g for nonporous carbon nanofiber to 235 m$^2$/g for porous carbon nanofibers. Accordingly, the cycling performance was improved from $\sim$350 mAh/g for nonporous carbon nanofibers to $\sim$500 mAh/g for porous carbon nanofibers (Figure 66).
To achieve higher capacity for carbon nanofibers, great efforts have been made to modify the carbon structures. Significant improvement was made by Huang’s group at Huazhong
University of Science and Technology, who obtained a super-high capacity and superior rate capability of carbon nanofiber in 2011.\textsuperscript{81}

In their work, polypyrrole (PPy) was selected as the carbon precursor because of the high nitrogen content (~16\%). After carbonization-activation process of PPy in nitrogen atmosphere with potassium hydroxide (KOH) as a porous activating agent, porous carbon nanofiber with nitrogen doping was obtained. It was reported that these carbon nanofiber exhibited a capacity of 943 mAh/g at 600\textsuperscript{th} cycle under a current density of 2000 mA/g.\textsuperscript{81} The electrochemical performance is shown in Figure 67. This is a great breakthrough for carbon materials as the anode in lithium-ion batteries. Therefore, doped carbon nanofibers deserve more attentions in future work.
Figure 67. Electrochemical performance of N-doped carbon nanofibers. (a) Cyclic voltammogram at a scan rate of 0.1 mV/s, (b) charge/discharge curves at 0.1 A/g, (c) cyclability and Coulombic efficiency at 2 A/g, and (d) capacity over cycling at different rates.\textsuperscript{81}

Inspired by those pioneering works, carbon nanofiber-based silicon composites have been developed for achieving higher energy density for lithium-ion batteries.

2.6.2 Carbon nanofiber-Si electrode design for lithium ion batteries

Carbon nanofiber-Si structures take the advantages of both good physical properties of carbon nanofibers and high electrochemical properties of silicon. Due to the significant volume change of silicon, carbon nanofibers are designated to host silicon and buffer its volume change and meanwhile to provide short electron and ion transport pathways.\textsuperscript{82,83} Therefore, the versatile design of carbon nanofiber-Si structure has received great attentions in the past four years.
It needs to point out that for carbon nanofiber-Si structure, silicon nanoparticles can be widely used since they are commercially available, industrially scalable, and compatible with most post-treatments. Although CVD silicon coated carbon nanofiber structure has been reported, the requirement for large amount of silicon loading at high expense hinders its industrial applicability.\textsuperscript{84,85}

The first silicon-containing carbon nanofiber (CNF-Si) electrode as anode for lithium-ion batteries was first reported by Zhang’s group at North Carolina State University in 2009. As-purchased silicon nanoparticles are added directly into the PAN solution with a controlled amount. Through electrospinning, silicon-containing PAN nanofibers can be obtained. Followed with thermal treatment, PAN-Si nanofibers turn into CNF-Si with a self-supported structure. CNF-Si with different silicon contents is shown in Figure 68.\textsuperscript{82} Large silicon agglomerates can be observed on the surface of carbon nanofibers. This is mainly due to the high surface energy that makes the serious agglomeration of silicon nanoparticles. The cycling performance is given in Figure 69.\textsuperscript{82} It showed high capacity but poor cycling stability. The fast capacity decay is attributed to the exposed silicon nanoparticles on the carbon nanofiber surface, which cannot be buffered by the carbon during the volume change, leading to the loss of silicon after several cycles. This problem becomes more severe when a high current density was applied. However, this new and inexpensive methods makes a breakthrough and brings a new concept of utilizing carbon nanofibers to motive the development of electrode design for lithium ion batteries.
Figure 68. Morphology of electrospun CNF-Si electrode for lithium ion batteries with different silicon contents. (a,b) 15 wt.%, (c,d) 30 wt.%, and (e,f) 50 wt.%.  

Figure 69. Cycling performance of electrospun CNF-Si with different silicon content (a-c) of 15, 30, and 50 wt.% at different current densities (A-D) with 50, 100, 150, and 200 mAh/g, respectively.
To further understand the failure mechanism and the limiting factors in designing anode materials based on silicon and carbon composites, Wang’s group at Pacific Northwest National Laboratory performed an n-depth study on the lithiation behavior of silicon nanoparticles and a carbon nanofiber composite by using the same electrospun CNF-Si sample provided from Zhang’s group. The morphologies of the CNF-Si composite are shown in Figure 70. According the images, the majority of silicon nanoparticles tend to aggregate to form clusters, which are either attached to the CNF surface or embedded into CNFs.

Figure 70. Morphologies characterizations of electrospun CNF-Si composite. (a) SEM image of overall view in which the silicon nanoparticles appear as white clusters. (b) SEM showing the cluster of silicon nanoparticles on a CNF. (c) TEM image showing the surface-attached silicon nanoparticles. (d) TEM image showing a cluster of silicon nanoparticles embedded in the CNF.
In order to observe the microstructural evolution of the CNF-Si induced by the volume expansion of silicon, *in situ* transmission electron microscopy (TEM) was used to capture the lithiation process of silicon within the CNF matrix. The TEM images at different steps of lithiation are compared in Figure 71.\(^8^6\) It was found that the lithiation of the embedded particle is delayed as compared with the particle attached to the carbon nanofiber surface, therefore limiting the rate performance of the battery.\(^8^6\) In addition, the lithiation of the embedded silicon can lead to the cracking of the carbon nanofibers, causing the disruption of the electrical conductivity of CNF-Si.\(^8^6\) The overall schematic of lithiation behavior of CNF-Si is given in Figure 72.\(^8^6\) This study may guide the design of carbon nanofiber and silicon nanoparticle composite as the electrode for lithium ion batteries.
Figure 71. Comparison of the lithiation characteristics of the particles attached to and embedded in the CNF. The lithiation of the embedded particles is delayed as compared with the particles attached to the carbon surface. Lithiation of the embedded particles leads to the cracking of the carbon fibers.
Figure 72. Schematic of lithiation of the silicon nanoparticles attached to and embedded in the CNF. (a) Initial structure. (b) Lithiation of the particles embedded in the CNF is delayed as compared with the particle attached to the surface of the CNF. Note the necking of the particles confined by the CNF. (c) Lithiation of the particles embedded in the CNF leads to the cracking of the CNF. Therefore, an ideal structure could be the confined silicon nanoparticles in a hollow carbon shell or embedding silicon nanoparticles in deformable carbon structure. The benefit of this design is that it can allow the volume expansion of silicon in a confined space and meanwhile to maintain the stable SEI formation on the interface between the carbon nanofiber and electrolyte. Followed by this design concept, representative work was done by Choi’s group at Korea Advanced Institute of Science and Technology and Cui’s group at Stanford University.
Choi’s group first introduced electrospun core-shell silicon-CNF structures as anode for lithium ion batteries. Dual-nozzle electrospinning is used to synthesize the core-shell structure, having mixture of silicon nanoparticles and polymethyl methacrylate (PMMA) as core and PAN as shell. After thermal treatment, PMMA was decomposed, leaving silicon encapsulated within the hollow carbon nanofiber structure. The schematic image is shown in Figure 73.

![Figure 73. Schematic illustration of the core-shell Si-CNF structure. (a) The electrospinning process using a dual nozzle. The PMMA solutions containing Si NPs and the PAN solution were injected into the core and shell channels of the nozzle, respectively. (b) After electrospinning, stabilization, and carbonization steps were employed to complete the core–shell 1D fibers consisting of Si NPs–C, respectively.](image)

The core-shell structure was well formed as shown in Figure 74. It is found that silicon nanoparticles can be fully embedded in the hollow sections of carbon nanofibers with a high silicon content. The heavy silicon loading in the composite may bring the issue of poor electrical conductivity for the densely packed silicon. In addition, the carbon fiber looks pretty
thick, with a large diameter of 1 μm, which may increase the electron and ion transport pathway.

**Figure 74.** Characterization of core-shell Si-CNF structure. SEM images of Si-CNF at (a) low and (b) high magnifications. (c) A cross-sectional SEM view of a single Si-CNF indicating that the core full of Si is wrapped by carbon shell. (d) A TEM image of a single Si-CNF. (Inset) A SAED pattern for the region in the white box with the diffraction rings indexed.88

The cycling performance is shown in **Figure 75.**88 Thanks to the confinement silicon nanoparticles in the CNF structure, stable cycling performance can be obtained. Therefore, according to this work, silicon-embedded carbon nanofiber structure is one of the effective way to achieve stable cycling performance for silicon-based electrodes.
In Cui’s work, a silicon-encapsulated hollow carbon nanofiber structure as developed.\textsuperscript{87} The schematic of the structure design is show in Figure 76. Carbon coating can help to maintain the stable SEI and the large empty space between silicon nanoparticles can sufficiently accommodate their huge volume changes during cycling to avoid the cracking of carbon materials.
Figure 76. Schematic of the silicon nanoparticles and carbon nanofiber design. (a) A conformal carbon coating on silicon nanoparticles will disintegrate due to the large volume changes experienced by Si nanoparticles during electrochemical reactions. (b) The carbon coating can be stabilized by designing an empty space inside the coating layer. The empty space allows for the free expansion and contraction of Si nanoparticles during lithiation and delithiation without any mechanical constrain or tension imposed on the Si nanoparticles. Thus, the empty space prevents damage to the carbon layer during Si volume changes.87

The fabrication and characterization of silicon-encapsulated carbon nanofiber structure is shown in Figure 77.87 Silicon-containing silica nanofibers are produced through electrospun process by using tetraethoxysilane (TEOS) as silica precursor. A carbon layer is then coated onto the as-prepared nanofibers by thermal carbonization of polystyrene. After removing silica, a structure with silicon nanoparticles encapsulated in hollow carbon nanofibers can be synthesized.87 Large empty space can be observed between silicon nanoparticles in the TEM images.
Figure 77. Fabrication of characterization of silicon nanoparticle-encapsulated carbon nanofiber structure. (a) Schematic outlining the material fabrication process. Si nanoparticles in SiO$_2$ nanofibers were first prepared by electrospinning. After carbon coating and removal of SiO$_2$ core, the Si@CNF structure was obtained. (b) SEM images of synthesized Si@CNF. (c) TEM images of synthesized samples. Lower inset shows TEM image with higher magnification; upper inset shows SAED pattern of the sample. (d) EDS spectrum of synthesized Si@CNF samples.$^{87}$

The electrochemical properties are shown in Figure 78.$^{87}$ This ideal structure makes a super-stable cycling performance in the 200 cycles, which is mainly because of the well intact hollow carbon nanofiber structure, which fully accommodates the expansion behavior of silicon. In addition, superior high rate capability of such electrode reflects the good electrical conductivity of carbon nanofibers.
Figure 78. Electrochemical characterizations of the silicon-encapsulated carbon nanofibers. (a) Charge–discharge cycling test of Si@CNF electrodes at a current density of 1A/g, showing 10% loss after 200 cycles. Dashed line indicates the theoretical capacity of traditional graphite anode. (b) Capacity retention of different Si nanostructures. (c,d) Galvanostatic charge–discharge cyclic curves of the first and later cycles of different Si nanoparticle-based electrodes: (c) Si@CNF electrode and (d) bare Si nanoparticle electrode. (e,f) Capacity retention (e) and galvanostatic charge/discharge profiles (f) of the Si@CNF electrode cycled at various current densities ranging from 0.8 to 8 A/g. All electrochemical measurements (a–f) were carried out at room temperature in two-electrode 2032 coin-type half-cells. Capacity is calculated based on the weight of total mass.

In needs to mention that their testing electrode was made by using a free-standing CNF-Si mat directly with no binder or conducting additives. This is important because the well-designed silicon-encapsulated hollow carbon nanofiber structure can be maintained intact, having no mechanical grinding to damage its structure. But the loading density, reported as 0.1 mg/cm², badly reduced the credibility of the electrochemical performance, especially the capacity value.
This is because the accuracy of specific capacity is much related to the mass of active material. Small silicon loadings cannot effectively reflect the electrochemical performance of electrode materials tested. Therefore, it is necessary to apply a high active material loading to illustrate the true electrochemical properties of as-made materials.
2.7 Carbon interlayer for lithium sulfur batteries

In this section, we will discuss the used of carbon structure as an interlayer for lithium sulfur batteries. Due to the fact that the concept of carbon interlayer has just been developed recently, it is a new area for the configuration of lithium sulfur batteries. The motivation and some representative work will be reviewed in this section and the prospects of carbon interlayer will be given.

2.7.1 The motivation of applying carbon interlayer to lithium sulfur batteries

For a conventional configuration of lithium sulfur batteries, it mainly consists of sulfur cathode, separator, and lithium metal anode. Originally, there was no carbon interlayer designed for the conventional lithium sulfur batteries. Most research groups are focusing on the encapsulation of sulfur to porous carbon structure or binder system design. In 2012, a porous carbon layer was first introduced to lithium sulfur batteries by S.S. Zhang at U.S. Army Research Laboratory.

A porous carbon cloth is sandwiched between the sulfur electrode and the separator, as shown in Figure 79. The sulfur can be dissolved into the liquid electrolyte in the form of polysulfide, and its migration between cathode and anode, known as shuttle effect, will consume lots of sulfur material, resulting in significant capacity loss and coulombic efficiency decrease. Thus, the introduction of porous cloth which functions as a catching layer that can increase the polysulfide migration length and provide additional conductive carbon surface area for polysulfide reaction sites. In Zhang’s design, this porous carbon cloth can absorb the dissolved
sulfur during the new cell’s storage as well as the dissolved polysulfide and meanwhile serve as the reaction sites for the reduction of the dissolved polysulfide.\textsuperscript{1,90} It was found that with the help of the carbon interlayer, the battery can have a longer shelf-life and exhibit similar capacity compared to the one without a carbon interlayer.\textsuperscript{90}

![Schematic configuration of a Li-S battery with a dual-layer structural sulfur cathode. Porous sulfur paper consisted of 90 wt.% sulfur and 10 wt.% binder.](image)

**Figure 79.** Schematic configuration of a Li-S battery with a dual-layer structural sulfur cathode. Porous sulfur paper consisted of 90 wt.% sulfur and 10 wt.% binder.\textsuperscript{90}

Therefore, carbon structure as an interlayer can play an important role in lithium sulfur batteries. More and more researchers will realize the importance of carbon interlayer and we believe it will attract more attentions in academic and industry in coming years.

### 2.7.2 Development of carbon interlayer for lithium sulfur batteries

As far as I know, only Manthiram’s group at University of Texas at Austin is now working on the effect of carbon interlayer on the electrochemical performance of lithium sulfur batteries. They independently introduced the concept of carbon interlayer in the Nature Communications in November 2012, which was seven months later than the publication of Zhang’s work in Journal of Power Sources.\textsuperscript{90,91}
In Manthiram’s work, they introduced an insertion of an electrolyte-permeable microporous carbon paper (MCP) between the separator and cathode disk to improve the electrochemical performance of lithium sulfur batteries, as shown in Figure 80 which is similar to Zhang’s work.\textsuperscript{90,91} The MCP was made of conductive carbon black and polymer binder.

\textbf{Figure 80.} Schematic and morphology of carbon paper employed in the lithium sulfur battery. (a) Schematic configuration of a battery with a bifunctional microporous carbon interlayer inserted between the sulfur cathode and the separator. (b) SEM image of the surface of the MCP and (c) transmission electron microscope image of the microporous carbon particles. The scale bars in b and c equal 500 nm and 10 nm, respectively.\textsuperscript{91}

With the insertion of the carbon interlayer, the electrochemical performance of the conventional sulfur cathode was greatly improved. The results are given in Figure 81.\textsuperscript{91} The impedance results shows a dramatic decrease in the charge transfer resistance, indicating the improved electrical conductivity of the sulfur electrode. The good rate capability and stable cycling performance demonstrated that the carbon layer could effectively capture the dissolved polysulfide and maximize the electrochemical properties of sulfur. Therefore, this bifunctional carbon interlayer can serve as a second current collector for accommodating the migrating active materials from sulfur cathode, which can not only simplify the battery processing with
no need of elaborate synthesis of sulfur-encapsulated composites and sulfur surface modification, but also improve the electrochemical performance, enabling its potential application in lithium sulfur batteries.\textsuperscript{91}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure81.png}
\caption{Electrochemical performance of carbon interlayer inserted lithium sulfur batteries. (a) Electrochemical impedance spectroscopy plots of Li–S cells with and without MCP, (b) cyclic voltammogram scans, (c) discharge/charge profiles at various cycles, (d) rate capability up to 3C and (e) cycle life and Coulombic efficiency of the cell with MCP at 1C and 2C for long cycles.\textsuperscript{91}}
\end{figure}
Followed by this main line, different forms of carbon interlayers, including CNT films, treated carbon paper, nickel form, nano-cellular carbon current collector, carbon nanofiber, porous carbon paper, and carbonized eggshell membrane, in lithium sulfur batteries were studied and 7 papers were reported from Manthiram’s group in the past one year.\textsuperscript{92–98} In the following, some representative examples will be reviewed and discussed.

The first one is a free-standing MWCNT paper as carbon interlayer for lithium ion batteries. The MWCNT paper was fabricated by the ultrasonic dispersion of MWCNT and then followed by vacuum filtration. The schematic cell configuration is shown in Figure 82, noticed that the sulfur cathode is on the bottom and lithium anode is on the top.\textsuperscript{92} It is claimed that the tortuous pores in the MWCNT paper can localize the polysulfide species diffusing from the cathode and because of its unique mechanical properties, the MWCNT skeleton is able to endure the volume change of the trapped active material during cycling. Due to the benefits of MWCNT, the sulfur battery gave a good cycling performance as shown in Figure 83.\textsuperscript{92}
Figure 82. Schematic of cell configuration having MWCNT paper as interlayer. (a) Traditional configuration with severe shuttle effect. (b) New configuration with MWCNT interlayer.  

Figure 83. Cycling performance of sulfur battery with and without MWCNT interlayer.  

It is noticed that there is no binder needed for the MWCNT interlayer, which is an improvement compared to the binder-mixed carbon black interlayer reported in their previous work. In my point, it is beneficial to the electrochemical properties of sulfur because that the binder-free structure can minimize the side reactions of the electrolyte and increase the electrical
conductivity and meanwhile prevent the deposition of the reduced polysulfide products onto the insulating area. However, the carbon interlayer needs to be accompanied with the sulfur cathode together. The unfavorable components in sulfur cathode, such as polymer binder and aluminum foil, can detrimentally influence the electrochemical properties of sulfur materials. Therefore, designing an integral cathode functioning as the sulfur cathode and carbon interlayer becomes importance to achieve high specific capacity and long cycle life.

To meet this goal, Manthiram’s team has recently developed a carbon membrane as a natural polysulfide reservoir to load the dissolved polysulfide catholyte as one integral cathode electrode. Their schematic design is shown in Figure 84. A free-standing carbonized sucrose-coated eggshell membrane (CSEM) was developed and used as Li$_2$S$_6$ catholyte reservoir to function together as the cathode electrode. The carbonized eggshell membrane acts as a porous frame and sucrose-derived carbon is used to provide good electrical conductivity. This structure can help to localize the catholyte within the cathode region to prevent the migration of polysulfide from cathode to anode. Because of the polysulfide reservoir, it shows a superior electrochemical performance given in Figure 85.
From the above-reviewed example, the carbon interlayer exhibits an important potential role in the new configuration of lithium sulfur batteries. It has been shown to be an effective way to improve the electrochemical properties of sulfur materials. However, future work should be focusing on the light-weight and integral sulfur-carbon interlayer structural cathode with high sulfur loading and high sulfur content. This is important because when speaking of the energy density of electrode, we must consider the total weight of the components. This means those high energy density as above-mentioned will be dramatically decreased by taking the mass of
the carbon interlayer into account. Therefore, to design an electrode with a truly high capacity is the most practical and important issue. 99
CHAPTER 3 EXPERIMENTS

3.1 Materials and Preparations

3.1.1 Carbon nanotube-based silicon nanostructures for lithium ion batteries

CNT forests were grown on a quartz substrate using iron chloride (FeCl$_2$) as the catalyst. Growth took place in a horizontal tube furnace (inner tube diameter around 6.8 cm) heated to 760 °C. Acetylene (C$_2$H$_2$), argon (Ar), and chlorine (Cl$_2$) gas were introduced to the chamber with flow rates of 600, 395, and 5 sccm respectively. The reaction took place at a reduced pressure of 3 Torr for 15 minutes. CNT sheets were drawn from the as-grown forests. The 10-layer CNT sheet (2 mg/cm$^3$) structures were placed onto a quartz substrate and then transferred into the horizontal tube furnace for silicon deposition. Silicon deposition was carried out using silane (SiH$_4$) gas (0.6% SiH$_4$ balance argon) as the silicon precursor at 10 Torr and 625 °C with a flow rate of 500 sccm for 1h. Those processing parameters were decided upon after initial testing showed them to produce the most uniform deposition throughout the CNT sheets. Higher temperatures led to an unwanted preferential deposition of silicon on the surface. To deposit carbon onto the silicon coated CNT sheet, the sample was heated directly to 760 °C after the silicon deposition step and then acetylene gas was introduced at a flow rate of 600 sccm at 20 Torr for 30 min. After the silicon and carbon deposition steps, the system was purged with Ar gas at a flow rate of 1000 sccm. The samples were taken out of the furnace when temperature fell below 100 °C.
3.1.2 Carbon nanofiber-based silicon nanostructures for lithium ion batteries

Polyacrylonitrile (PAN) (Mw = 150,000 g/mol, Aldrich) was used as the carbon precursor for carbon nanofiber. Silicon nanoparticles (diameter: 30-50 nm) were purchased from Nanostructured & Amorphous Materials, Incorporated. N, N-dimethylformamide (DMF, Aldrich) was used as the organic solvent for electrospinning. All these chemicals were used without further purification.

The PAN solution consisted of 8 wt.% PAN in DMF. Silicon nanoparticle dispersions were made by adding silicon nanoparticles in the PAN polymer solution. The dispersions were prepared and applied with strong mechanical stirring at 60 °C for 24 hours and then applied with ultra-sonication for 1 h before electrospinning. The as-prepared dispersions were then electrospun into nanofibers with a flow rate of 0.75 ml/h at 1.5 kV. Note that details of further treatment of silicon and carbon nanofiber are mentioned in the following chapters.

The as-prepared nanofibers were stabilized in air at 280 °C for 5.5 hours (heating rate: 5 °C min\(^{-1}\)) then carbonized at 760 °C in argon for 1 hour (heating rate: 2 °C min\(^{-1}\)) to obtain composites.

3.1.3 Carbon nanofiber-based sulfur nanostructures for lithium sulfur batteries

Polyacrylonitrile (PAN) (Mw = 150,000 g/mol, Aldrich) was used as the carbon precursor for carbon nanofiber. N, N-dimethylformamide (DMF, Aldrich) was used as the organic solvent for electrospinning. All these chemicals were used without further purification.
The PAN solution consisted of 8 wt.% PAN in DMF. The PAN solution were then electrospun into nanofibers with a flow rate of 0.75 ml/h at 1.5 kV. The as-prepared nanofibers were stabilized in air at 280 °C for 5.5 hours (heating rate: 5 °C min⁻¹) then carbonized at 760 °C in argon for 1 hour (heating rate: 2 °C min⁻¹) to obtain composites. Note that details of further treatment of carbon nanofiber are mentioned in the following chapters.

Elemental sulfur (Aldrich) was placed in the center of heating zone of tube furnace. The as-prepared CNF was loaded in the end of heating zone of tube furnace. Argon gas was flowed into the furnace with a rate of 17 sccm through the whole experiment.

3.2 Characterizations

3.2.1 Structure characterization

The morphologies of the samples were investigated using a field emission scanning electron microscope (FE-SEM, JEOL 6400F) and transmission electron microscope (TEM, HITACHI HF2000, accelerating voltage 200 kV). The crystallographic and chemical structures were studied using wide angle X-ray diffraction (WAXD, Rigaku Smartlab) and a Renishaw Raman microscope (514 nm). Compositions of samples were examined by variable pressure scanning electron microscope (VPSEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The surface analysis was surveyed by X-Ray Photoelectron Spectroscopy (XPS).
3.2.2 Electrochemical evaluation

*Lithium ion batteries*

Working electrodes were prepared by punching the as-prepared films directly into disks with diameter of 0.5 inch. The electrode mass was measured on a balance with a resolution of 0.01 mg. The counter electrode was lithium ribbon (99.9%, Aldrich). The electrolyte used was 1 M LiPF$_6$/ethylene carbonate (EC) + dimethyl carbonate (DMC) + diethyl carbonate (DEC) (1:1:1 by volume, MTI Corporation). The 2032 coin cells were assembled in a high-purity argon-filled glove box. All the cells were tested using a LAND-CT 2001A battery test system.

*Lithium sulfur batteries*

Working electrodes were prepared by punching the as-prepared films directly into disks with diameter of 0.5 inch. The electrode mass was measured on a balance with a resolution of 0.01 mg. The counter electrode was lithium ribbon (99.9%, Aldrich). The electrolyte was prepared by 1 M lithium bis(trifluoromethanesulfonyl) imide/1,2-dimethoxyethane and 1,3-DOL (1:1 by volume, Aldrich) containing LiNO$_3$ (1 wt%). The 2032 coin cells were assembled in a high-purity argon-filled glove box. All the cells were tested using a LAND-CT 2001A battery test system.
CHAPTER 4 EFFECT OF CVD CARBON COATINGS ON SI@CNF COMPOSITE AS ANODE FOR LITHIUM-ION BATTERIES

ABSTRACT

Lithium-ion battery (LIB) anodes with high capacity and binder free structure were synthesized from carbon nanofibers that contained silicon nanoparticles (Si@CNF). The particle filled nonwoven structures were produced by an electrospinning and subsequent carbonization process. Pristine Si@CNF composites had Si nanoparticles exposed on the fiber surface. As produced, the Si nanoparticles could become detached from the nanofiber surface during cycling, causing severe structural damage and capacity loss. In order to prevent Si from detaching from the nanofiber surface, the Si@CNF composite was then treated with a thermal chemical vapor deposition (CVD) technique to make Si completely coated with a carbon matrix. The carbon coated Si@CNF (Si@CNF-C) composites were synthesized with different Si contents (10, 30, and 50 wt.%) for different CVD treatment times (30, 60, and 90 min). It was found that the initial coulombic efficiency of Si@CNF-C could be increased via the amorphous carbon by stabilizing solid-electrolyte-interface (SEI) formation on surface. The capacity and cyclic stability were improved by the CVD carbon coating, especially for the 30 wt.% Si@CNF-C composite with 90 min CVD coating, a CVD amorphous carbon coating of less than 1% by weight on Si@CNF composites contributed to more than 200% improvement in cycling performance. Results indicate that the CVD carbon coating is an effective approach to improve the electrochemical properties of Si@CNF composites making this a potential route to obtain high-energy density anode materials for LIBs.
**Keywords**: Lithium-ion battery anode, Silicon, Carbon nanofibers, CVD, SEI, Coulombic efficiency

### 4.1 Introduction

Lithium-ion batteries (LIBs) have been used in the portable electronic market for over 20 years due to their high energy density and flexible design. High-performance LIBs are now needed for transportation applications and grid storage systems. To meet the high capacity requirements of these large-scale applications, researchers have put significant effort into exploring new materials and designing novel structures for high-energy density LIBs.\(^4\,6\,100^\)

Graphite is a commercial anode material for LIBs due to its low cost, low flat working potential and long cycling performance. However, the theoretical capacity for graphite is only 372 mAh/g,\(^101^\) which is not sufficient to meet the high energy-storage demands in the transportation and grid storage applications. Therefore, significant attention has been focused on researching new anode materials with higher capacities to replace the graphite anode structure in LIBs.

Silicon (Si) has an extremely high theoretical capacity of ~4200 mAh/g and is a promising anode material for next-generation LIBs. However, the large volumetric change (up to 400%) of Si during charge and discharge causes serious pulverization and loss of electrical contact between active materials (i.e., Si), conducting agents (i.e., carbon black), and even the current collector. The large volume change of Si can also cause the structural failure of the active materials and accelerate the formation of solid electrolyte interphase (SEI), resulting in reduced capacity and poor cycling life.\(^102^\) In order to maintain the structural integrity of the active
materials and the electrodes, several strategies have been used. One is to reduce the Si particle size to the nanoscale so that mechanical fracture can be avoided through strain relaxation, to minimize the cracking and pulverization of Si and electrodes. The second strategy is to introduce a buffer matrix to accommodate the Si volumetric change during cycling. Graphite and carbon nanofibers are good choices to host Si because their good flexibility, high electronic conductivity, large surface area, open pore structure, and good electrochemical stability. The carbon matrix also helps form a stable SEI film on the electrode surface. However, the traditional techniques of fabricating Si-based electrodes could reduce the volumetric and gravimetric energy densities due to the introduction of polymer binders. Hence, one promising approach to address this challenge is to design binder-free Si-carbon composite electrodes for high-energy LIBs.

Recently, Si nanoparticle-contained carbon nanofiber (Si@CNF) composites have been developed, which combine the advantages of silicon (high capacity) and carbon (good electrical conductivity and excellent structural stability). Si@CNF composites were synthesized by electrospinning a Si nanoparticle filled polymer solution and subsequent carbonization of the nanofiber mats. The free-standing, electrically-conductive Si@CNF mats can be cut into appropriate sizes to be used directly as binder-free, high-energy electrodes. However, Si@CNF composites have not reached their performance potential due to the exposure of some of the Si nanoparticles on the fiber surfaces. These exposed Si nanoparticles can react with the electrolyte directly, resulting in heavy SEI formation. Without carbon protection, the Si nanoparticles detach from the nanofiber surfaces after several cycles, causing
severe fiber damage and capacity loss. In this work, a chemical vapor deposition (CVD) technique was introduced to coat disordered carbon on the surface of Si@CNF composites. The carbon coating was able to protect the exposed Si on the nanofiber surface and strengthen the mechanical bonding between carbon nanofiber surface and Si nanoparticles. Results show that the carbon coating improved the initial coulombic efficiency and cycle performance of Si@CNF composites. The CVD carbon coating provides a simple and fast means to obtain high-energy, stable anodes for advanced LIBs.

4.2 Experimental

4.2.1 Nanofiber Preparation

Polyacrylonitrile (PAN) (Mw = 150,000 g/mol, Aldrich) was used as the carbon precursor for the Si@CNF composites. Si nanoparticles (diameter: 30-50 nm) were purchased from Nanostructured & Amorphous Materials, Incorporated. N, N-dimethylformamide (DMF, Aldrich) was used as the organic solvent for electrospinning. All these chemicals were used without further purification.

The PAN solution consisted of 8 wt.% PAN in DMF. Silicon nanoparticle dispersions were made with increasing amounts (10, 30, and 50 wt.%) of Si nanoparticles in the polymer solution. The dispersions were prepared and applied with strong mechanical stirring at 60 °C for 24 hours and then applied with ultra-sonication for 1 h before electrospinning. The as-prepared dispersions were then electrospun into Si@PAN nanofibers with a flow rate of 0.75 ml/h at 1.5 kV.
The as-prepared Si@PAN nanofibers were stabilized in air at 280 °C for 5.5 hours (heating rate: 5 °C min⁻¹) then carbonized at 760 °C in argon for 1 hour (heating rate: 2 °C min⁻¹) to obtain Si@CNF composites. The nanofiber composites were then coated with carbon via CVD through the thermal decomposition of acetylene (C₂H₂) as the carbon precursor gas. The deposition occurred at 760 °C, 600 sccm flow rate of acetylene while the system was maintained at 20 torr. These conditions allowed for a relatively slow but uniform deposition of the carbon on the very high surface area Si@CNF mats. Si@CNF-C composites with different thickness of carbon coatings were obtained with different CVD treatment times (30, 60, and 90 min).

### 4.2.2 Structure Characterization

The morphology of Si@CNF-C composites was investigated by field emission scanning electron microscope (FE-SEM, JEOL 6400F) and transmission electron microscope (TEM, HITACHI HF2000). The structure of Si@CNF-C composites was studied by wide angle X-ray diffraction (WAXD, Rigaku Smartlab) and a Renishaw Raman microscope.

### 4.2.3 Electrochemical Evaluation

The electrochemical properties were tested using CR 2032 coin cells. Si@CNF-C composites were free-standing, conductive nanofiber mats, and they were directly used as the working electrode without the addition of binder material or conducting agent. The average thickness and weight of the working electrode were around 0.232 mm and 4.10 mg, respectively. The counter electrode was lithium ribbon (99.9%, Aldrich). The electrolyte used was 1 M
LiPF$_6$/ethylene carbonate (EC)+dimethyl carbonate (DMC)+diethyl carbonate (DEC) (1:1:1 by volume, MTI Corporation). Coin cells were assembled in a high-purity argon-filled glove box. All the cells were tested at a current density of 50 mA/g with cut-off potentials between 0.01 and 2.0 V using a LAND-CT 2001A battery test system. The cyclic voltammetry (CV) tests were carried out by a Gamery reference 600 Potentiostat/Galvanostat/ZRA device with scanning rate of 0.05 mV/s in the potential window of 0.01 to 2.00 V.

4.3 Results and Discussions

4.3.1 Morphology and Structure

![Diagram](image)

**Figure 86.** Design of Si@CNF-C composite. (a) Schematic of Si@CNF-C composite. (b-c) SEM images of 10 wt.% Si@CNF and Si@CNF-C composite with 90 min carbon coating time. (d) Photographs of Si@CNF-C composite with 90 min carbon coating time. Inset shows good flexibility of the composite.
Figure 86a shows a schematic of Si@CNF-C composite. The pristine Si@CNF composite had Si nanoparticles exposed on the surface. These exposed Si nanoparticles can form a heavy SEI and detach from the CNF during cycling. In comparison, the carbon layer on the Si@CNF-C composites protects the Si nanoparticles and helped to stabilize the SEI. Figure 1B-C present the SEM images of both pristine 10 wt.% Si@CNF composite and 10 wt.% Si@CNF-C composite with 90 min coating time. Si nanoparticles were observed on carbon nanofiber surface. From the SEM images, the surface morphology of Si@CNF and Si@CNF-C were similar and CVD carbon coating could not be observed clearly by using SEM. Si@CNF-C composite with a self-sustained structure shows good flexibility (Figure 86d).
Figure 87. TEM images of 10 wt.% Si@CNF-C composites with different coating times: (a) 0 min, (b) 30 min, (c) 60 min, and (d) 90 min.

Figure 87 shows TEM images of 10 wt.% Si@CNF-C with different carbon coating times. For comparison, the TEM image of pristine Si@CNF composite is shown in Figure 87a. It is seen that in all four samples, not all of the Si nanoparticles were completely embedded in carbon nanofibers; some of Si nanoparticles were exposed in agglomerates on the nanofiber surface. The pristine Si@CNF composite showed no carbon coating on the exposed Si nanoparticles. Si@CNF-C composites with 30, 60, 90 min carbon coating times clearly show amorphous carbon coatings on the Si nanoparticle surfaces (Figure 87b-d). The carbon coating became more and more rough and a ridge-like structure was formed for the Si@CNF-C
composite with 90 min coating time. The thickness of the carbon coating increased, on average, from 10 nm, 15 nm, to 17 nm, respectively, when the carbon coating time increased from 30, 60, to 90 min.

Figure 88. (a) WAXD patterns, (b) Raman spectra, and (c) XPS spectra of 10 wt.% Si@CNF-C composites with different CVD coating times.

The X-ray diffraction (XRD) analyses of Si@CNF-C composites with different CVD coating times are shown in Figure 88a. For the pristine Si@CNF (i.e., 0 min coating time), diffraction peaks at 2θ of 29°, 47°, 56°, 69° and 76° were indexed as the (1 1 1), (2 2 0), (3 1 1), (4 0 0) and (3 3 1) planes of Si crystals, respectively.\textsuperscript{82,107} With the introduction of the CVD coating and increase in CVD time, the intensities of Si peaks were weakened by the amorphous carbon coating. The weak and broad (0 0 2) diffraction peak at 2θ =25° was ascribed to the disordered carbon structure.\textsuperscript{108} This indicates that both the carbon nanofiber and CVD carbon coating had a disordered structure, which was further confirmed by Raman spectroscopy.

Raman spectra of Si@CNF-C composites with different carbon coating times are shown in Figure 88b. Two typical carbon peaks can be observed: one is the D-band (1360 cm\textsuperscript{-1}), which
is associated with sp³-bonded amorphous carbons or interstitial defects\textsuperscript{109}, and the other is the G-band (1582 cm\textsuperscript{-1}), corresponding to the in-plane stretching vibration mode of E\textsubscript{2g} graphitic crystallites of carbon.\textsuperscript{108,109} The relative intensity ratio (i.e., R-value) of D-band to G-band is used to characterize the degree of disorder in the structure of carbon materials. A larger R-value indicates a higher degree of disorder. The R-value of Si@CNF-C composites increased from 0.93 to 1.02, 1.10 and 1.15, respectively, with increasing carbon coating time (0, 30, 60, 90 min). Results indicate that the carbon coating generated by CVD using C\textsubscript{2}H\textsubscript{2} gas was more disordered than the carbon nanofiber matrix generated by the carbonization of PAN precursor. The rough surface of composites after CVD carbon coating could explain the increased R-value. With an increase in the carbon coating time, the mass of disordered carbon deposited on Si@CNF composites increased as well.

X-ray photoelectron spectroscopy (XPS) was utilized to examine the Si@CNF-C composites to determine whether the Si nanoparticles were fully covered by the carbon coating (Figure 88c). The pristine Si@CNF composite exhibited two major peaks related to Si element: one assigned to Si at 99.5-100 eV and the other assigned to oxidized Si at 103-104 eV. Oxidized Si mainly came from the oxidized layer on Si nanoparticles (i.e., silicon dioxide). For the Si@CNF-C composite with 30 min carbon coating time, the Si peaks were detected but had a lower intensity. This was mainly due to the influence of relatively low thickness (10 nm) and non-uniformity of the carbon coating. With an increase in the thickness of carbon coating after either the 60 or 90 min treatment time, the Si nanoparticles were fully covered with a layer thick enough that Si signal could no longer be detected.
4.3.2 Electrochemical Performance

Figure 89. Galvanostatic charge-discharge profiles of 10 wt.% Si@CNF-C composites with different CVD coating times: (a) 0 min, (b) 30 min, (c) 60 min, and (d) 90 min.

Galvanostatic charge-discharge tests were conducted to evaluate the electrochemical performance of the Si@CNF-C composites. Figure 89 shows the charge-discharge profiles of the initial two cycles of Si@CNF-C composites (10 wt.%) with different CVD coating times.
Table 3 Capacity, efficiency and capacity retention of 10 wt.% Si@CNF-C composites with different CVD coating times

<table>
<thead>
<tr>
<th>760 °C CVD carbon coating time</th>
<th>0 min</th>
<th>30 min</th>
<th>60 min</th>
<th>90 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>First-cycle discharge capacity (mAh/g)</td>
<td>1330.5</td>
<td>1234.4</td>
<td>1245.4</td>
<td>1212.6</td>
</tr>
<tr>
<td>First-cycle charge capacity (mAh/g)</td>
<td>880.9</td>
<td>923.4</td>
<td>918.5</td>
<td>925.9</td>
</tr>
<tr>
<td>First-cycle irreversible capacity (mAh/g)</td>
<td>449.6</td>
<td>311</td>
<td>326.9</td>
<td>286.7</td>
</tr>
<tr>
<td>First-cycle coulombic efficiency (%)</td>
<td>66.2</td>
<td>74.8</td>
<td>73.7</td>
<td>76.4</td>
</tr>
<tr>
<td>Second-cycle capacity retention (%)</td>
<td>65.7</td>
<td>74.2</td>
<td>76.0</td>
<td>78.1</td>
</tr>
</tbody>
</table>

The capacity, coulombic efficiency and capacity retention values of composites are shown in Table 3. The first-cycle charge capacity and the corresponding initial coulombic efficiency were increased with the increasing time of CVD carbon coating. These improvements can be explained by the contribution of amorphous carbon coating in constraining the Si within carbon matrix and helping to reduce the SEI formation on the electrode surface during the electrochemical reactions. Figure 89a shows a long voltage plateau at 0.6 V in the first
discharge curve. This behavior is generally explained to be an effect of the continuous decomposition of liquid electrolyte and the formation of SEI film at the electrode-electrolyte interface. As shown in Figure 89b-d, with an increase in coating time, the voltage plateau at 0.6 V shortened and gradually transitioned to a smooth curve with no apparent plateau, indicating that the intensity of side electrochemical reactions (e.g., electrolyte decomposition and formation of SEI) was weakened by the carbon coating. This result can be contributed to the different SEI products. In general, the SEI film formed in prismatic areas of graphite mainly consists of inorganic compounds (Li$_2$CO$_3$-abundant) with gaseous by-products, which are unstable, while the SEI film formed in basal planes is enriched with organic compounds, which are more compact and relatively stable. Hence, the SEI formation is significantly affected by the morphology of the carbon coating surface.

Figure 90. High-magnification TEM images of Si@CNF-C composites with different CVD coating times: (a) 30 min, (b) 60 min, and (c) 90 min. The arrow indicates basal planes of CVD carbon coating.
For the Si@CNF-C composite, basal planes of CVD carbon coating can be observed in the high-magnification TEM images (Figure 90). These basal planes could help to stabilize the SEI by forming compact and stable organic compounds on the surface, leading to short voltage plateau and improved initial coulombic efficiency. For the pristine Si@CNF composite, no basal planes of PAN-based carbon can be observed and it is believed that unstable inorganic compounds were generated within disordered carbon matrix due to intensive solvent reduction, which in turn leads to long voltage plateau and decreased initial coulombic efficiency in the first lithiation process. Therefore, the CVD carbon coating on the Si@CNF-C surface acted as a protecting layer to stabilize SEI formation and contribute to improved coulombic efficiency.

Figure 91. CV of (a) 10 wt.% Si@CNF composite and (b) 10 wt.% Si@CNF-C composite with 90 min carbon coating time. The scanning rate was 0.05 mVs⁻¹ in the potential window of 0.01 -2.00 V.

To better understand the effect of carbon coating on the initial electrochemical process, cycle voltammetry (CV) was performed on the 10 wt.% Si@CNF-C sample with 90 minute CVD carbon treatment (Figure 91). Two reversible peaks at around 1.25-1.30 V were present in both CV spectra of pristine Si@CNF and Si@CNF-C composites. These peaks correspond to
the lithiation and delithiation processes of disordered carbon materials. The anodic peak at 0.25 V and the cathodic peaks at 0.31 V and 0.49V were present due to the two-phase transition corresponding to the lithiation and delithiation process of Li-Si alloys. Present in Figure 6A, the broad peak between 0.75 and 0.5 V is commonly linked to the electrochemical reactions of decomposing electrolytes, indicating the formation of SEI. The same peak for the Si@CNF-C sample with 90 min coating time became smaller and narrower compared with the large and broad peak of pristine Si@CNF. This change further demonstrates that the electrolyte decomposition and SEI formation was reduced.

![Graph showing cycle performance](image)

**Figure 92.** Cycle performance of 10 wt.% Si@CNF-C composites with different CVD coating times. The cycle performance of 10 wt.% Si@CNF-C composites with different coating times is shown in Figure 92. For the pristine Si@CNF composite, the charge capacity decreased to 570 mAh/g at the 30th cycle with a capacity retention of 65%. With the addition of the carbon
coating, all three Si@CNF-C composites with different CVD coating times showed improved capacity of around 700 mAh/g with 76% capacity retention at 30th cycle. Without the carbon coating, exposed Si nanoparticles were prone to fall off from the nanofiber due to the large volume change of Si during cycling. The improvement was mainly attributed to the confinement of the Si nanoparticles by the continuous carbon coating.

Figure 93. SEM images of (a-b) 10 wt.% Si@CNF composite and (c-d) 10 wt.% Si@CNF-C composite with 30 min carbon coating after 30 cycles.

Cells were disassembled to analyze the surface morphology change of pristine 10 wt.% Si@CNF and Si@CNF-C (30 min coating) composites at the fully charged state after 30 cycles (Figure 93). While both uncoated and carbon coated showed damage from volume change of the Si during cycling, the imaging revealed that there was a subtle improvement in the
morphology exhibited by the coated samples. Figure 93a-b shows the Si@CNF composite and the damage produced where Si nanoparticles were originally located. Due to the repeated large volume expansion and contraction of Si, carbon nanofibers could not accommodate the volume change so that Si nanoparticles either fell off from their original locations or irreversibly damaged the CNF. In Figure 93c-d although vacant holes were observed, many Si nanoparticles were preserved and attached on the fibers surface with SEI maintained. This further indicates that carbon coating helped restrict Si nanoparticles in carbon matrix during cycling.

To obtain higher capacities, Si@CNF-C composites with higher Si contents (greater than 10 wt.%) were fabricated and studied. Higher Si content could accelerate the structural failure of the nanofibers due to the intensified volume change of Si within clusters. Therefore, the carbon coating became more important for the Si@CNF composites with higher Si content. Figure 94 shows the charge-discharge profiles and cycle performance of 30 wt.% Si@CNF-C composites with different carbon coating times. These composites exhibited similar electrochemical results to the 10 wt.% Si@CNF-C composites. The initial coulombic efficiency increased from 73.6%, 81.4% to 83.0% when the CVD coating time increased from 0, 30 to 90 min, respectively. The voltage plateau in the first discharge curve became smaller and smoother with increase in carbon coating time. In addition, the cycle performance also improved with the introduction of the CVD carbon coating. For 30 wt.% Si@CNF-C with 90 min carbon coating, the charge capacity was preserved above 1000 mAh/g at 30th cycle, which was much larger than that (around 300 mAh/g) of 30 wt.% Si@CNF at the same cycle.
Figure 94. Galvanostatic charge-discharge profiles of 30 wt.% Si@CNF-C with different coating times: (a) 0 min, (b) 30 min, and (c) 90 min, and (d) the corresponding cycle performance.
Figure 95. Galvanostatic charge-discharge profiles of 50 wt.% Si@CNF-C with different coating times: (a) 0 min, (b) 30 min, (c) 90 min, and (d) the corresponding cycle performance.

Figure 95 shows the charge-discharge profiles and cycling performance of 50 wt.% Si@CNF-C composites. The initial coulombic efficiency improved from 68.7%, 84.7% to 85.3% when the CVD carbon coating increased from 0, 30 to 90 min, respectively. The voltage plateau in the first discharge curve was significant for Si@CNF composite, but was greatly reduced after the 90 min CVD carbon coating. The cycling performance also improved after the CVD carbon coating, although significant capacity loss was still observed even with 90 min CVD carbon coating. When the Si content was 50%, too much volume change occurred that amorphous carbon could not hold Si and buffer the volume change any more, leading to the huge capacity loss after several cycles. These results inspire us to apply heavier amorphous carbon coatings.
to Si@CNF composites with smaller Si nanoparticles to enhance the constraining effect for Si in our future study.

4.4 Conclusions

Novel Si@CNF-C composites were prepared as binder-free anodes for LIBs by the electrospinning and subsequent carbonization of Si nanoparticle dispersions in PAN solutions, followed by a CVD carbon coating. It was found that the CVD carbon coating improved the initial coulombic efficiency because it helped stabilize the SEI films by forming organic compounds on the basal planes of carbon coating layers. The carbon coating was also able to provide mechanical bonding between Si and carbon to constrain Si nanoparticles in their originally locations, and this effect helped maintain the structural stability of the electrodes, leading to higher capacities and improved cycle performance. Results showed that compared with Si@CNF composite, the capacities at the 30th cycle were improved by 36%, 200%, and 80%, respectively, for 10, 30 and 50 wt.% Si@CNF-C composites with the 90 min carbon coating time. We successfully demonstrated that CVD carbon coating on Si@CNF surfaces provides a promising strategy to obtain binder-free anode materials for high-energy LIBs.
5.1 Introduction

To meet requirements of high capacity and long cycle life, researchers have devoted great attentions to exploring new materials with novel structures for lithium ion batteries (LIBs). Graphite, because of its capability to store one lithium for every six carbon atoms as LiC₆, has been widely used as anode with a theoretical capacity of 372 mAh/g in lithium ion batteries. Compared with graphite, one mole of silicon (Si) can accommodate 3.75 moles of lithium and consequently get a capacity of 3579 mAh/g at room temperature. The ten folds higher capacity of silicon shows a promising potential to take the place of graphite for the next-generation lithium ion batteries.

Despite the high lithium storage capability of silicon, its 300% volume change upon lithium alloying and de-alloying processes presents a major problem to the electrochemical properties and cycling performance of silicon electrode. For silicon particles, not only will particles undergo pulverization but also its electrode composite be detrimentally damaged due to the significant volume change of silicon. The cracks and pulverizations will leave silicon particles lose electrical contacts and thus directly result in poor electrochemical performance of silicon electrode. In addition, solid-electrolyte-interphase (SEI) films will be formed on fresh surface of silicon after its volume expansion and surface cracking, leading to extra electrolyte consumption and electrical insulation of electrode.
Recently, many efforts have been made to improve silicon electrochemical performance by incorporating silicon nanoparticles with carbon structures, including carbon coatings, graphene stacking, carbon nanotube (CNT) entanglement, and carbon nanofiber (CNF) confinement. It has been well demonstrated that their electrochemical performance can be greatly improved by employing a proper spatial correlated carbon matrix to silicon nanoparticles. Since the facile synthesis and flexible design of CNF, especially for electrospun polyacrylonitrile (PAN)-derived carbon nanofiber, CNF and silicon (CNF-Si) composite attracts considerable attentions to the development of long cycling life and high capacity of silicon composite electrode. As an important component of silicon composite electrode, CNF outperforms three key characteristics over other carbon structures: (a) high lithium storage capacity, (b) self-constructed flexible structure, and (c) good electrolyte retention. Thus carbon nanofiber will provide an ideal conductive matrix to host silicon nanoparticles as CNF-Si composite electrode. Typical design is a core-shell structure with engineered empty space to sufficiently accommodate the silicon volume change and meanwhile stabilize SEI films. Their good cycling performance confirms the important role of hollow structure in the cycling stability of CNF-Si composite. However, given the viability of the synthesis and loading density of CNF-Si electrode, a more practical strategy is in great need to produce high loading density and low cost CNF-Si electrode.

In this project, we designed a flexible and self-supporting carbon-enhanced CNF mat with confined vacant space that encapsulates Si nanoparticles (vacant Si@CNF@C) to be used as the anode in LIBs. Electrospinning and chemical vapor deposition (CVD) techniques were
used for the synthesis of this composite, which are common industrial techniques. The confined vacant space was designed to accommodate the increasing volume of Li-Si and SEI during lithium insertion while containing any pulverize Si to minimize the dramatic capacity loss of the electrode. When comparing with different CNF-based Si electrodes, the vacant Si@CNF@C exhibited the best charge-discharge capabilities in terms of good cycling performance (620 mAh g$^{-1}$), high coulombic efficiency (99%), and good capacity retention (80%) after 200 cycles.

5.2 Experimental

5.2.1 Preparation of Si@SiO$_2$

200 mg Si nanoparticles (30-50 nm, Nanostructured & Amorphous Materials) were dispersed in a mixture solution of 350 mL ethanol and 100 mL water. After 1 hour sonication, 5 mL ammonium hydroxide was dropped into the solution with vigorous stirring. Then 3.5 g tetraethoxysilane (TEOS, Aldrich) was dropped into the solution with mechanical stirring and kept at room temperature overnight. After centrifugation and washing with DI water, the as-prepared Si@SiO$_2$ particles were dried in vacuum oven for 12 hours.

5.2.2 Fabrication of vacant Si@CNF@C composites

Polyacrylonitrile (PAN) (Mw = 150,000 g/mol, Aldrich) was used as the carbon precursor for the CNFs. Si@SiO$_2$ (10 wt.%) was dispersed in an 8 wt.% PAN solution in DMF. The as-prepared dispersion was then electrospun into Si@PAN nanofibers with a flow rate of 0.75 ml/h at 1.5 kV. The as-prepared nanofibers were stabilized in air at 280 °C for 5.5 hours.
(heating rate: 5 °C min\(^{-1}\)) and then carbonized at 760 °C in argon for 1 hour (heating rate: 2 °C min\(^{-1}\)) to obtain the Si@SiO\(_2@CNF\) composite fabrics. The nanofiber composite was then coated with carbon via CVD through the thermal decomposition of acetylene (C\(_2\)H\(_2\)) as the carbon precursor gas. The deposition occurred at 760 °C, 600 sccm flow rate of acetylene while the system was maintained at 20 torr for 30 min. These conditions allowed for a relatively slow but uniform deposition of carbon on the nanofiber surface. The as-prepared nanofibers were then soaked in 10 wt.% hydrofluoric acid (HF) aqueous solution for 5 hours to remove the SiO\(_2\). After cleaning in DI water and drying in an oven, the vacant Si@CNF@C composite was obtained. For comparison, solid Si@CNF and vacant Si@CNF composite fabrics were also prepared.

### 5.2.3 Structure Characterization

The morphology of nanofibers was investigated using a field emission scanning electron microscope (FE-SEM, JEOL 6400F) and transmission electron microscope (TEM, HITACHI HF2000, accelerating voltage 200 kV) equipped with selected area electron diffraction (SAED). The crystallographic and chemical structures were studied using wide angle X-ray diffraction (WAXD, Rigaku Smartlab) and a Renishaw Raman microscope (514 nm).

### 5.2.4 Electrochemical Evaluation

The vacant Si@CNF@C nanofibers formed a conductive, free-standing mat that was punched directly into binder-free disk-like electrodes with diameter of 0.5 inch. The counter electrode used was lithium ribbon (99.9%, Aldrich). The electrolyte used was 1 M LiPF\(_6\)/ethylene
carbonate (EC) + dimethyl carbonate (DMC) + diethyl carbonate (DEC) (1:1:1 by volume, MTI Corporation). The 2032 coin cells were assembled in a high-purity argon-filled glove box. All cells were tested with cut-off potentials between 0.01 and 2.0 V using a LAND-CT 2001A battery test system. The coulombic efficiency was calculated as the ratio of the capacity for Li insertion to the capacity for the Li extraction.

5.3 Results and Discussions

5.3.1 Morphology and Structure

Figure 96. Schematic design of vacant Si@CNF@C composite. SiO$_2$ was coated on Si nanoparticles by hydrolysis of TEOS. The as-prepared Si@SiO$_2$ nanoparticles were electrospun into PAN nanofibers followed by carbonization and CVD carbon coating. After removing the SiO$_2$ with HF acid, confined vacant spaces were created for the Si nanoparticles.

The procedure for synthesizing the vacant Si@CNF@C composite is shown in Figure 96. Tetraethoxysilane (TEOS) as silicon dioxide (SiO$_2$) precursor was used to grow silica coatings on Si nanoparticles.$^{123}$ The as-prepared Si@SiO$_2$ nanoparticles were electrospun into
polyacrylonitrile (PAN) nanofibers followed by carbonization (760 °C) to obtain Si@SiO\textsubscript{2} nanoparticle-filled carbon nanofiber (Si@SiO\textsubscript{2}@CNF) mat. The as-prepared nonwoven mat was then coated by amorphous carbon via CVD technique to obtain Si@SiO\textsubscript{2}@CNF@C. During the CVD coating, the carbon precursor, acetylene (C\textsubscript{2}H\textsubscript{2}) gas, was introduced with a flow rate of 600 sccm at 760 °C for 30 min. After the CVD coating process, any Si particles that were initially partially exposed on the fiber surface then became completely coated with carbon\textsuperscript{85}. The confined vacant space was created after removing SiO\textsubscript{2} through exposure to hydrofluoric (HF) acid. After cleaning with deionized water and drying in oven, the vacant Si@CNF@C composite nonwoven mat was ready for electrochemical testing.
Figure 97. Morphological characterization of vacant Si@CNF@C composite. (a) TEM image of Si@SiO$_2$ nanoparticles. (b) TEM image of a vacant Si@CNF@C nanofiber. (c-d) SEM images of a vacant Si@CNF@C nanofiber mat with low and high magnifications. (e) Photograph showing excellent flexibility of the vacant Si@CNF@C nanofiber mat. (f) As-punched disk as a binder-free electrode for coin-type lithium-ion cell.
**Figure 97** shows the morphological characterization of the vacant Si@CNF@C composite. For comparison, a TEM image of Si@SiO2 nanoparticles is shown in **Figure 97a**. It is seen that the as-prepared Si@SiO2 nanoparticles exhibit a clear core-shell structure. Diameters of the as-prepared Si@SiO2 nanoparticles were around 100 - 200 nm, in comparison with the 30 - 100 nm diameter of pristine Si nanoparticles. Vacant space can be observed clearly after removing the SiO2 coating from the nanoparticles embedded in the CNF matrix (**Figure 97b**). Due to the agglomeration of Si@SiO2 nanoparticles, a continuous tunnel-like vacant space was created within the CNFs encapsulating the Si particles. The size of the vacant space can be manipulated by adjusting the thickness of SiO2 coating through TEOS treatment. Here, the size of vacant space created is larger than the size of pristine silicon nanoparticles, which can provide sufficient to accommodate silicon 300% volume expansion. In a previous study, it was found that nano particles are often attached to or partially embedded in the carbon nanofibers to form Si clusters, which can deteriorate the carbon matrix during Si volume expansion leading to structural failure of the fibers and rapid capacity loss.86 In this work, the amount of Si@SiO2 nanoparticles, the thickness of SiO2 coating and the thickness of CVD carbon coating were controlled to obtain a good vacant Si@CNF@C structure as shown in **Figure 97c-d**. This self-supported and binder-free composite shows good flexibility as shown in **Figure 97e**. It can endure several cycles of a hand bending test without obvious fracture. The nonwoven mat can be used as an electrode directly without current collector or polymer binder. This structure can be promisingly applied to the flexible batteries. In the battery testing, the nonwoven silicon composite were cut directly into disks fitting for the 2032 coin-type cells (**Figure 97f**). The average mass of the electrode used in this work was 1.43 mg/cm².
Figure 98. Characterizations of Si@SiO\textsubscript{2} nanoparticles and vacant Si@CNF@C composite. (a) FT-IR spectrum of Si@SiO\textsubscript{2} nanoparticles. (b) Raman spectra (Silicon) of Si and Si@SiO\textsubscript{2} nanoparticles. SiO\textsubscript{2} was grown on Si surface. (c) Raman spectra (Silicon) of Si@SiO\textsubscript{2}@CNF@C composite and vacant Si@CNF@C composite. (d) Raman spectrum (Carbon) of vacant Si@CNF@C composite. D-band peak is higher than G-band peak, indicating the amorphous structure of carbon-coated CNF. (e) XRD pattern of vacant Si@CNF@C composite.

The characterization of Si@SiO\textsubscript{2} nanoparticles as well as their corresponding composites was carried out using Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, and X-ray diffraction (XRD) techniques (Figure 98). In the FT-IR spectrum of Si@SiO\textsubscript{2} nanoparticles (Figure 98a), the SiO\textsubscript{2} coating can be confirmed by the characteristic peaks of bending and stretching of Si-O-Si bonds at 798 and 1081 cm\textsuperscript{-1}, respectively. The small shoulder at 1200 cm\textsuperscript{-1} is related to different vibration mode of SiO\textsubscript{2}. The peaks at 950 and
1632 cm\(^{-1}\) come from the residual of TEOS.\(^{125}\) Si@SiO\(_2\) nanoparticles were further analyzed by Raman spectroscopy as shown in Figure 98b. As control, pristine Si nanoparticles were examined and they showed a sharp peak of around 520 cm\(^{-1}\), indicating the crystalline nature of Si.\(^{126}\) For the Si@SiO\(_2\) nanoparticles, a characteristic peak of the D\(_1\) defect from sol-gel derived silica (SiO\(_2\)) was detected at around 500 cm\(^{-1}\), confirming the presence of SiO\(_2\) coating on the Si surface.\(^{127}\) After incorporation into the CNF matrix and coated with CVD carbon, the Raman spectra of the resultant vacant Si@CNF@C composite as well as Si@SiO\(_2\)@CNF@C composite (before HF etch) are shown in Figure 98c. Both Si and SiO\(_2\) were detected before HF etching. After HF etching, only the crystalline Si peak was present, indicating the complete removal of SiO\(_2\) coating. In Figure 98d, the Raman spectrum (carbon) of the vacant Si@CNF@C composite exhibited a high R-value (>1), which is the ratio of D band (1340 cm\(^{-1}\)) intensity to the G band (1580 cm\(^{-1}\)) intensity, indicating a disordered structure of the CNF matrix and CVD carbon coating. The disordered carbon and crystalline silicon structures of the vacant Si@CNF@C were also confirmed by the XRD spectrum in Figure 98e.
5.3.2 Electrochemical Evaluations

Figure 99. Electrochemical characterization of various types of Si and CNF composites. Galvanostatic charge-discharge profile of (a) PVdF-assisted Si electrode, (b) solid Si@CNF, (c) vacant Si@CNF, and (d) vacant Si@CNF@C composites. (e) Cycle performance and (f) coulombic efficiencies of different types of Si nanoparticle-based electrodes.
Electrochemical properties of the vacant Si@CNF@C composite were tested in 2032 coin cells by using lithium metal foil as the counter electrode for charging and discharging in the voltage range of 0.01 - 2 V vs. Li+/Li at 100 mA h⁻¹. The results of this testing are shown in Figure 99. For comparison, traditional binder-assisted Si electrode was tested as the control (Figure 99a). It was prepared by mixing Si nanoparticles with polyvinylidene fluoride (PVdF) polymer binder and carbon black (8:1:1 by weight). The PVdF-assisted Si electrode had charge and discharge capacity of 873 and 3264 mAh g⁻¹, respectively with a low coulombic efficiency (CE) of 27%, through the first cycle. After the 5th cycle, charge capacity dropped rapidly to 400 mAh g⁻¹ with almost 54% capacity loss. This is a common phenomenon for PVdF binder-assisted silicon electrode. The PVdF polymer cannot effectively hold silicon and carbon additives together, thus leading electrode to lose mechanical and electronic connection. In addition, the ionic conductivity of silicon will be negatively influenced by the polymer coating on surface. Thus, binder-free structure provides one possibility to solve concerns of mechanical adhesion, electronic connection, and ionic retention existing in the conventional binder system of silicon electrode. Confining Si nanoparticles in the CNF can provide an effective way to address those challenges seen in binder-assisted Si electrodes. In addition to the vacant Si@CNF@C composite electrode, other forms of CNF-based electrodes, i.e., solid Si@CNF (composites with pristine silicon nanoparticles) and vacant Si@CNF (SiO₂-removed composites without CVD carbon coatings), were also synthesized and tested. The specific capacities for the composite electrodes were calculated based on the total mass of Si, CNF, and carbon coating if any. The solid Si@CNF composite exhibited charge and discharge capacities of 855 and 1302 mAh g⁻¹, respectively, with a CE of 66% through the first cycle (Figure 99b).
The charge capacity decreased to 738 mAh g\(^{-1}\) with a 16% capacity loss at the 5\(^{th}\) cycle. In the solid Si@CNF composite, CNF cannot be sufficiently confine the nanoparticle and provide a buffer zone for the expansion of the Si, even to Si particles that are fully embedded within the CNF. For the vacant Si@CNF composite, the initial charge and discharge capacities reached 977 and 1890 mAh g\(^{-1}\), respectively with a CE of 51.7% (Figure 99c). High irreversible capacity was observed in the 2\(^{nd}\) lithiation process, indicating that excessive electrolyte was consumed due to the formation of heavy SEI. At the 5\(^{th}\) cycle, charge capacity was remained at 598 mAh g\(^{-1}\), with a capacity loss of 39%. This dramatic capacity loss can be ascribed to the detachment of Si nanoparticles from the opening of porous CNF matrix during Si volume expansion and extraction process. This can be attributed to the large number of particles that reside on the fiber surface after spinning and carbonization. Among all electrodes studied, the vacant Si@CNF@C composite demonstrated the best charge-discharge properties (Figure 99d). Its initial charge and discharge capacities were 780 and 1328 mAh g\(^{-1}\), respectively, with a CE of 58.7%. As compared to the vacant Si@CNF composite without CVD carbon coating, the area under the curve of electrolyte reduction/degradation stage (~0.7V) became smaller for the vacant Si@CNF@C composite, indicating that less electrolyte participated in the formation of SEI. At the 5\(^{th}\) cycle, vacant Si@CNF@C composite exhibited a capacity retention of 81% retention with the capacity value of 632 mAh g\(^{-1}\), which was the higher among all electrodes studied.

The cycling performance and coulombic efficiencies are shown in Figures Figure 99e-f, respectively. The binder-assisted Si electrode showed rapid capacity decay and its charge
capacity was only 153 mAh g\(^{-1}\) at the 50\(^{th}\) cycle, which is not acceptable for the long cycle life requirement of practical batteries. For comparison, the performance of pure carbon nanofibers is also shown. Results showed that pure carbon nanofibers exhibited a higher charge capacity of 300 mAh g\(^{-1}\) at 50\(^{th}\) cycle, which is still not satisfactory. It is also seen that both electrodes showed large variations in the coulombic efficiencies during the cycling. For solid Si@CNF, vacant Si@CNF, and vacant Si@CNF@C composites, they exhibited different cycle behaviors during the 200 cycles. The capacity of solid Si@CNF declined to 216 mAh g\(^{-1}\) at the 200\(^{th}\) cycle, with a capacity retention of 25%. The corresponding coulombic efficiency increased from 65.6% to 98.0% in the beginning 13 cycles, followed by an apparent decrease to 95.8% at around 40\(^{th}\) cycle. After that, the coulombic efficiency increased again and eventually maintained at 99.0% in the following cycles. The dramatic coulombic efficiency change of solid Si@CNF can be ascribed to the volume change of Si nanoparticles during cycling. In addition, a small bump occurred in the cycling curve of solid Si@CNF composite, which is correlated to the bowl shape of CE curve in the first 50 cycles. Such correlated capacity and coulombic efficiency changes may be the result of the lithiation delay of the embedded Si compared with the attached Si on the CNF as well as the detachment of Si from the CNFs.\(^{86}\) For the vacant Si@CNF composite, the cycling curve exhibited a fast capacity loss trend. The charge capacity decreased from 978 to 414 to 320 mAh g\(^{-1}\) at 50\(^{th}\) and 200\(^{th}\) cycle, respectively. The corresponding CE value increased from 52% to 99% quickly in the first 10 cycles and maintained above 99.5% in the following cycles. The short time needed to achieve high CE value (>99%) indicates that porous CNF could facilitate the contact between Si and electrolyte and eliminate the lithiation delay of embedded Si caused by the blocking effect of CNF matrix.
However, due to the lack of protection to the Si, the Si nanoparticle detachment significantly reduced the capacity and there were only 51%, 42%, and 32% capacity retained at 10th, 50th, and 200th cycle, respectively. Along with heavy SEI growth in the electrode, the vacant Si@CNF composite suffered severely structural failure and fast capacity fading. The carbon coating that was applied as the final layer on the vacant Si@CNF@C composite was designed to address those issues.

After the CVD carbon coating, the vacant Si@CNF@C composite showed a significant improvement in the cyclic stability, coulombic efficiency (>99%), and capacity retention (80%), demonstrating the enhanced confinement of silicon nanoparticles in the empty chamber. As shown in Figure 99c, the capacity decreased from 780 to 612 mAh g\(^{-1}\) in the first several cycles, and then it kept increasing to 784 mAh g\(^{-1}\) until the 85th cycle. After that, the capacity only experienced a slight decrease and a relatively high capacity of 620 mAh g\(^{-1}\) was achieved at the 200th cycle. Correspondingly, the CE curve of vacant Si@CNF@C showed a different trend compared with that of vacant Si@CNF composite. The CE increased from 58.7% at the 1st cycle to 99.2% at the 12th cycle and it remained above 99% until 99.7% at the 51st cycle. Then, the CE curve had slightly decrease to 98.5% at 95th cycle and kept increasing to 99.9% in the following 100 cycles. It took only several cycles for the vacant Si@CNF@C composite to achieve a high CE value (>99%), which was similar to the vacant Si@CNF. This further confirms that porous CNF provides direct contact between Si and electrolyte in the confined vacant space. During cycling, along with the increase in capacity in the first 85 cycles, it is observed that the CE value decreased slightly, following by a continuous increase. The
capacity delay is possibly due to the large empty chamber of carbon nanofiber, which increases the distance for lithium to diffuse through the carbon to reach the embedded silicon nanoparticles. In addition, part of the accumulated silicon nanoparticles can contact with the carbon, resulting in less activation of silicon in the beginning of several cycles. During the repeatedly volume expansion and pulverization, more particles are activated and thus capacity will increase accordingly. On the other hand, the decrease in CE may come from more SEI formation on the pulverized Si. It is envisioned that continued growth of SEI on Si pulverized within the vacant space may still exceed the free volume needed and thus begin to rupture the CNF or CVD carbon coating, resulting in the final capacity fade. Similar behaviors have been found in different Si-carbon core-shell structure materials, but few researchers have given attention to this phenomenon.
Figure 100. Electrode morphology before and after electrochemical cycling. TEM images of (a) pristine vacant Si@CNF@C electrode and cycled electrodes after (b) 100 cycles and (c) 200 cycles. (d) Schematic of Si evolution in the Si@CNF@C electrode: i. silicon nanoparticles are in the empty chamber of carbon nanofiber, ii. SEI is initially covered on surfaces, iii. SEI is continuously produced on the pulverized silicon and gradually fill up the empty chamber, iv. finally, SEI productions exceed the carbon chamber wall and silicon nanoparticle are no longer confined.

Although some researchers have used in-situ methods to observe the lithiation of Si as well as its composites, it is still challenging to examine the structural evolution of vacant Si@CNF@C composite in the long range of battery cycling. In this work, we dissembled batteries through different cycles to observe the morphology change of the silicon composite using TEM. Prior to TEM observation, the cycled electrode was washed by HCl to remove SEI. Figure 100a shows the vacant Si@CNF@C structure before cycling. The confined vacant
space as well as Si can be clearly observed. After cycling, the CNF suffered damages and the resultant morphology is dependent on the cycle number. Figure 100b shows a representative image of what the structure of vacant Si@CNF@C looked like after 100 cycles. The entire vacant space of CNF was occupied with opaque substances. These substances may have been the pulverized Si and remaining decomposed electrolyte. This was probably due to the continuous SEI growth accompanied with Si pulverization that gradually took up the whole space. When the vacant holes have no remaining space to accommodate the SEI growth and Si pulverization, the new generated SEI and pulverized Si will eventually break the thin carbon walls and destroy the vacant CNF structure as shown in Figure 100c. After 200 cycles, the CNF matrix was severely damaged, therefore capacity kept decreasing. The schematic interpretation of this process is shown in Figure 100d to describe the Si evolution in the vacant CNF structure. In the first lithiation process, large SEI was formed on both outside and inside surfaces of the carbon chamber of fibers (ii). During cycling, the pulverization of Si resulted in more surface area for SEI formation. After prolonged cycling, the carbon chamber was filled up with SEI and pulverized Li-Si and the filling material began to expand the CNF and the confined vacant space became smaller (iii). Eventually, continuous SEI growth as well as the expansion of Si broke the carbon chamber and the pulverized silicon would expose to electrolyte directly with no carbon protection any more (iv). According to these observations and analyses, We have to admit that, in the final, capacity decreasing and carbon chamber breaking are inevitable due to the continuously SEI growth. Therefore, the key for the design of the spatial-related silicon-carbon nanofiber composite is to avoid Si agglomeration and achieve silicon fully embedded into carbon nanofibers, then to design large enough chamber
to accommodate the 300% volume expansion of silicon and the increasing growth of SEI, so as to postpone SEI productions exceeding the limited volume of empty space and realize the long cycling life and high capacity.

### 5.4 Conclusions

In summary, we have successfully designed and fabricated composite anodes of CNFs with confined vacant spaces containing Si nanoparticles. This material is a flexible and binder-free electrodes produced by electrospinning and CVD techniques. Compared to other forms of Si@CNF composites, the resultant vacant Si@CNF@C exhibited excellent properties in terms of cycle performance (620 mAh g\(^{-1}\) at 200th cycle), coulombic efficiency (99%), and capacity retention (80%) in 200 cycles. The confined vacant space can accommodate the huge volume expansion of Li-Si and the formation of SEI while preserving the pulverized nanoparticles to prevent dramatic capacity loss and extend the Si cycle life for hundreds of cycles. This design can be also extended to other materials suffering from large volume change issues during energy storage.
CHAPTER 6 ALIGNED CARBON NANOTUBE-SILICON SHEETS: A NOVEL
NANO-ARCHITECTURE FOR FLEXIBLE LITHIUM-ION BATTERY
ELECTRODES

6.1 Introduction

In the pursuit of high performance lithium-ion batteries (LIBs), significant effort has been
expended to explore high performance cathode and anode materials.\textsuperscript{3,6,7,42,119} Silicon (Si) has
the greatest lithium storage capacity per unit mass, and is therefore one of the most promising
potential candidates to replace graphite as the anode material in future generations of
batteries.\textsuperscript{102,130} The main challenge in utilizing silicon comes from the structural failure induced
by its huge volume change (>300\%) during electrochemical cycling, leading to capacity
loss.\textsuperscript{131} Significant efforts have been made to improve the electrochemical cyclic stability of
silicon by engineering the micro- and nano-structure.\textsuperscript{132} Nano-size silicon materials combined
with carbon in the form of nanoparticles,\textsuperscript{82,117} nanowires,\textsuperscript{133,134} nanotubes,\textsuperscript{135} and nanofibers,\textsuperscript{7}
have been studied, all demonstrating good electrochemical performance. The combination of
carbon with the silicon structure is intended to provide good electrical conductivity and
superior chemical and electrochemical stability, and also to work as a coating layer to maintain
structural integrity by buffering the large silicon volume change.\textsuperscript{42,104} New designs in which
silicon and carbon can act in a mutually beneficial way so that silicon can fully contribute to
the capacity while maintaining cyclic stability are needed.
The small diameter, high surface area, electrical conductivity and graphitic structure of carbon nanotubes (CNT) have led to their use in energy storage applications. Depositing silicon coatings onto CNT (CNT-Si) is an effective way to utilize the desirable traits of both CNT and silicon. Due to their unique properties, CNT assemblies can provide an ideal scaffold for loading active electrodes materials while the structure can be tailored to accommodate the volume fluctuation during cycling. Electrodes are traditionally prepared in a slurry-casting method in which slurry, having a binder polymer/conducting agent and anode active material, is cast onto copper foil. CNT-based active material is generally mixed with binder and current collector to make binder-assisting electrode. The non-electrochemically active binders and current collector can account for a large mass fraction of the electrode, dramatically reducing the overall energy density of the battery. In binder-free designs, all of the components are electrochemically active, maximizing the specific capacity potential. Recent studies have reported different CNT-Si structures as flexible and binder-free electrodes for high-energy density batteries. CNTs can provide a continuous electron pathway for the silicon coatings if they are constructed into a network before silicon deposition. An ideal flexible anode structure containing silicon coated CNTs should contain the following structural characteristics: 1) no binder, 2) no current collector, 3) flat flexible film with low density of conducting material, 4) non-bundled CNTs with sufficient porosity to allow for uniform Si coating on individual CNTs, and 5) an aligned CNT structure for controlled volumetric expansion of silicon during cycling. Previous studies have touched on a few of these important characteristics. The anode architecture developed in this work address all of these
important characteristics through the use of self-sustained super-aligned CNT sheets as the silicon scaffold.

In this work, we present an aligned CNT-Si sheet structure, which is a free-standing, binder-free and flexible anode. The super-aligned CNT sheet acts as the current collector and an electrochemically active substrate upon which the silicon active material is deposited. The aligned CNT structure provides significant inter-tube space for the uniform deposition of silicon coatings through the thickness of CNT sheet and accommodates the silicon expansion during cycling.

6.2 Experimental

6.2.1 Preparation of CNT-Si and CNT-Si-C

CNT arrays were grown on a quartz substrate using iron chloride (FeCl₂) as the catalyst. Growth took place in a horizontal tube furnace (inner tube diameter around 6.8 cm) heated to 760 °C. Acetylene (C₂H₂), argon (Ar), and chlorine (Cl₂) gas were introduced to the chamber with flow rates of 600, 395, and 5 sccm respectively. The reaction took place at a reduced pressure of 3 Torr for 15 minutes. CNT sheets were drawn from the as-grown arrays. The 10-layer CNT sheet structures were placed onto a quartz substrate and then transferred into the horizontal tube furnace for silicon deposition. Silicon deposition was carried out using silane (SiH₄) gas (0.6% SiH₄ balance argon) as the silicon precursor at 10 Torr and 625 °C with a flow rate of 500 sccm for 1h. Those processing parameters were decided upon after initial testing showed them to produce the most uniform deposition throughout the CNT sheets.
Higher temperatures lead to an unwanted preferential deposition of silicon on the surface. To deposit carbon onto the silicon coated CNT sheet, the sample was heated directly to 760 °C after the silicon deposition step and then acetylene gas was introduced at a flow rate of 600 sccm for 30 min. After the silicon and carbon deposition steps, the system was purged with Ar gas at a flow rate of 1000 sccm. The samples were taken out of the furnace when temperature fell below 100 °C.

6.2.2 Structure Characterization

The morphologies of the samples were investigated using a field emission scanning electron microscope (FE-SEM, JEOL 6400F) and transmission electron microscope (TEM, HITACHI HF2000, accelerating voltage 200 kV) equipped with selected area electron diffraction (SAED). The crystallographic and chemical structures were studied using wide angle X-ray diffraction (WAXD, Rigaku Smartlab) and a Renishaw Raman microscope (514 nm). Compositions of samples were examined by variable pressure scanning electron microscope (VPSEM) equipped with energy-dispersive X-ray spectroscopy (EDS).

6.2.3 Electrochemical Evaluation

Working electrodes were prepared by punching the as-prepared films directly into disks with diameter of 0.5 inch. No binder or current collector was used for preparing the electrodes. Typical electrode mass was 0.4-0.5 mg. The electrode mass was measured on a balance with a resolution of 0.01 mg. The counter electrode was lithium ribbon (99.9%, Aldrich). The electrolyte used was 1 M LiPF₆/ethylene carbonate (EC) + dimethyl carbonate (DMC) +
diethyl carbonate (DEC) (1:1:1 by volume, MTI Corporation). The 2032 coin cells were assembled in a high-purity argon-filled glove box. All the cells were tested with cut-off potentials between 0.01 and 1.0 V using a LAND-CT 2001A battery test system. The coulombic efficiency (CE) was calculated as the ratio of the capacity for Li insertion to the capacity for the Li extraction.

6.3 Results and Discussions

6.3.1 Morphology and Structure

Figure 101. Schematic of CNT-Si sheet structure. Vertical-grown aligned CNT arrays drawn into aligned CNT sheets. The self-supported CNT sheet was coated with Si as the main active anode material for the LIBs. A continuous CNT-Si core-sheath structure was obtained.

Figure 101 shows a schematic of the super-aligned CNT-Si sheet composite. Vertical aligned CNT arrays were grown on quartz substrates and were drawn horizontally out from the arrays to fabricate the continuous aligned CNT sheets. The width of CNT arrays can be controlled by the size of quartz substrate. The CNT sheet drawn for this study was approximately 6 cm wide.
Figure 102. Procedures of synthesizing CNT-Si and CNT-Si-C sheets. (a), Wide, continuous aligned CNT sheet was drawn from a CNT array and rolled on a cylinder. (b), Photo image of the CNT sheet. CNT sheet was placed onto a quartz plate for CVD silicon coating. (c), Photo image of CNT-Si sheet. The color changed from black to brown, indicating successfully Si coating. (d), Photo image of CNT-Si sheet. The self-sustained CNT-based structure shows good flexibility. (e), Free-standing and binder-free electrode for lithium-ion cell testing.

Figure 102 shows the steps taken to produce the aligned CNT sheet and CNT-Si sheet composite. The CNT sheet was first taken up onto a copper foil-covered roller until the structure was 10 CNT sheet layers thick (Figure 102a). The 10-layer CNT sheet was then placed onto a quartz stage for silicon chemical vapor deposition (CVD) treatment (Figure 102b). Silane (SiH₄) gas (0.6% SiH₄, balance argon) was the silicon precursor and was introduced into the furnace with a flow rate of 500 sccm at 625 °C. The pressure was maintained at 10 Torr for 1 h to obtain the silicon deposited CNT sheets. The black color of the CNT sheet material changed to brown, indicating a silicon coating was present (Figure 102c). The self-sustained CNT structure showed good flexibility after coating (Figure 102d).
Some of the as-prepared core-shell CNT-Si composites were then coated with an additional layer of carbon (CNT-Si-C). The carbon precursor, acetylene (C₂H₂) gas, was introduced into the furnace with a flow rate of 600 sccm at 760 °C for 30 min after the silicon deposition step. It is possible to integrate the composite sheet into a rolled or stacked battery cell directly without using any binder or metal current collector. Due to the fact that the CNT sheets were drawn off the array in a continuous fashion, it is feasible to expect that the silicon deposition process and collection of the sheet material could be engineered into a roll-to-roll process for commercial battery production. In our case, disks (diameter: 12.5 millimeters) were punched out and used as the anodes in coin cells (Figure 102e).

Figure 103. Structures of CNT-Si and CNT-Si-C sheets. SEM (a-b) and TEM (c) images of the CNT-Si sheet. SEM (d-e) and TEM (f) images of the CNT-Si-C sheet. Uniform silicon coating was observed on the super-aligned the CNT sheet. Schematic images of CNT-Si and CNT-Si-C structure (g).
The morphology of the composites was determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The top surfaces of the CNT-Si and CNT-Si-C sheets are shown in Figure 103a and 3d, respectively. The alignment of the CNTs within the sheet is clearly observed. Some curved CNTs were observed bridging across those paralleled ones and through different layers, which could facilitate the electron transfer between layers.\textsuperscript{140} The original CNT-to-CNT contacts in the sheet remain after the deposition of the silicon. Higher magnification SEM images (Figure 103b) showed that the silicon coating was uniformly deposited on the CNTs. Compared with the as-grown diameter of the CNTs (10-50 nm), the diameter of the silicon coated CNTs reached 300 nm. The TEM image of the CNT-Si material (Figure 103c) shows that the silicon film was composed of very small silicon grains (20-40 nm). For the CNT-Si-C sheet structure, the diameter of each individual coated CNT was around 250 nm with enlarged silicon grains linked together (Figure 103e). The thin pyrolytic carbon coating (20 nm thick) was deposited on the surface of the silicon coating which contained the larger silicon grains (100-200 nm) (Figure 103f). The change in the crystallite size of silicon before/after the carbon coating was mainly caused by the high temperature used during the carbon deposition which transformed small silicon grains into larger ones by the annealing process.\textsuperscript{130,141,142}
Figure 104. Characterizations of CNT-Si and CNT-Si-C sheets. (a), Raman spectra of CNT-Si and CNT-Si-C to examine Si. (b), Raman spectra of CNT, CNT-Si and CNT-Si-C to examine carbon. (c), X-ray diffraction of CNT-Si and CNT-Si-C sheets.

The CVD silicon and carbon materials were characterized using Raman spectroscopy and X-ray diffraction (XRD) techniques. In Figure 104a, the peak centered at 497 or 509 cm\(^{-1}\) is related to the silicon Raman phonon vibration. Typical characteristic peaks for amorphous and crystalline silicon are centered at ~480 cm\(^{-1}\) and at ~520 cm\(^{-1}\), respectively. As the crystallite size decreases, the crystalline silicon peak shifts to lower wavenumbers.\(^{143–146}\) For the CNT-Si-C sample, the silicon peak centered at 509 cm\(^{-1}\) was sharper with higher intensity compared with the broad silicon peak present in the CNT-Si sample. The different shapes of the two silicon peaks reveal larger crystallites of silicon were formed during the deposition of the disordered carbon, confirming the TEM result. Characteristic peaks of carbon are shown in the Raman spectra as D (disordered carbon) and G (graphitic carbon) peaks in Figure 104b. The pristine CNT sheets showed a high G/D intensity ratio (G/D value: 2.3), indicating the graphitic nature of the large diameter multiwall CNTs. After the silicon coating, the intensity decreased and the G peak shifted to a lower wavenumber. The weakened intensity was due to the thickness of silicon coating. The downshift of G peak has been previously explained in terms
of structural disorder and defects of carbon structures.\textsuperscript{147} The impaired CNT should be caused by the silicon coating, which is possibly due to the formation of interfacial amorphous carbon layer between CNTs and silicon in the coating process.\textsuperscript{66} Although such interfacial carbon layer cannot be observed directly because of the conformal Si coating, the Raman results demonstrates that the CNT structure (sp\textsuperscript{2}) might be partially damaged where the amorphous carbon interlayer formed, resulting in the downshift of the G band to a lower wavenumber. The CNT-Si-C sheet exhibited a lower G/D ratio (G/D value: 1.0), confirming that disordered carbon was deposited on the silicon surface. An up shift of the G peak was also observed for those samples. Annealing composite structures containing carbon at high temperature can lead to the upshift of the G band to a higher frequency due to compressive stresses on the carbon structure.\textsuperscript{148} The sp\textsuperscript{2} bonds in the CNT walls may experience compressive forces due to the different thermal expansion coefficients of materials (Si, CNT, and amorphous carbon), causing the Raman in-plane vibrational E\textsubscript{2g} phonon shift to a higher wavenumber.\textsuperscript{148} Figure 104c shows the XRD pattern of the CNT-Si sheet. The small peak next to the sharp graphite peak (002) is assigned to silicon (111), indicating the low crystallinity of the silicon in the CNT-Si sheet. In comparison, the graphite peak has a much lower intensity than that of silicon (110) after the carbon deposition step. This transition is in agreement with the TEM and Raman results.
In order to confirm that the change in crystallinity was due only from the high temperatures needed for the carbon deposition, the CNT-Si sheet was treated using the same conditions needed for the carbon deposition, except that acetylene flow was replaced with argon. The XRD pattern (Figure 105) showed typical sharp peaks of graphite and silicon with high intensities, confirming that it was the high processing temperature during the carbon deposition step that led to the increase in crystallinity of the silicon coating.

### 6.3.2 Electrochemical Evaluation

The CNT-Si and CNT-Si-C sheet anodes were assembled in 2032 coin cells using lithium metal foil as the counter electrode. Galvanostatic charge-discharge profiles of the CNT-Si sheet anodes, based on a 50 mA g⁻¹ current density, are shown in Figure 106a.
Figure 106. Electrochemical characteristics of CNT-Si and CNT-Si-C sheets. Performance of CNT-Si. Galvanostatic charge-discharge profiles (a), differential capacity curves (b), and cycle performance at 50 mA/g in the potential range of 0.01-1.0 V (c). Performance of CNT-Si-C. Cycle performance at 100 mA/g (d) and rate capability cycled at different current densities (e) in the potential window of 0.01-1.0 V.

The CNT-Si sheet reached 3322 and 2487 mA g⁻¹ for their discharge and charge capacities, respectively, with an initial coulombic efficiency (CE) of 75%. In comparison, the first discharge and charge capacities were 2270 and 1801 mA g⁻¹, respectively, with an initial CE of 79% for the CNT-Si-C sheet (Figure 107).
**Figure 107.** Electrochemical characteristics of CNT-Si-C. Galvanostatic charge-discharge profiles (a), differential capacity curve (b), and cycle performance (c) of CNT-Si-C at 50 mA/g in a potential window of 0.01-1.0 V.

This improvement of CE was attributed to the outer-layer of pyrolytic carbon. The charging-discharging curves present two voltage plateaus developed during first lithiation process of the CNT-Si sheet anodes, one at 1.15 V and the other one at 0.4 V. These two voltage plateaus are generally linked to the electrolyte decomposition and SEI formation. Differential capacity curves (dQ/dV vs. V) were used to study the lithiation and delithiation processes of the silicon. For the CNT-Si sheet anodes (Figure 106b), a small broad lithiation peak at 0.27 V with a small peak at ~0.30 V were present. These peaks are related to the lithium ion alloying reaction with amorphous silicon. The following large peak at 0.12 V corresponded to the lithiation of crystalline silicon. A flatter first lithiation voltage indicates a two-phase type reaction and the higher voltage slope of the subsequent cycle indicates a one-phase reaction. Hence, the silicon coatings showed similarities in the electrochemical properties to other researchers’ results. Cycle performance of the CNT-Si sheet anodes is shown in Figure 106c. Good cyclic stability was observed with no dramatic capacity loss. Multiple studies have shown that as compared to
crystalline silicon, amorphous silicon shows better cycle performance due to the homogeneous lithium insertion resulting in less silicon pulverization. The amorphous nature of the Si and the aligned CNT sheet structure helped to mitigate the stresses induced by the volume change, leading to the cyclic stability of CNT-Si sheet. The CE of CNT-Si sheet anodes stabilized at 96.8% after 30 cycles. This trend is in agreement with a similar study where silicon coated CNT arrays were used as a LIB anode structure. It is desired to have the highest efficiency possible. Lower coulombic efficiency indicates larger irreversible capacity, which is linked to the structural failure of the electrode material. Repeated formation of SEI on silicon surfaces, exposed by pulverization after each cycle, can decrease the CE. During the volume change in cycling, small nanoparticles in the silicon coatings may separate from each other and even detach from the CNT, which further reduces the lithium capacity, resulting in a lower efficiency. It has been demonstrated that carbon coatings on silicon nano-structures can effectively improve the CE by constraining the silicon and forming a stable SEI layer.

Our CNT-Si-C sheet anodes showed an increase in cycle performance stability with a higher CE (>97%). A higher current density (100 mA g⁻¹) was used for testing the CNT-Si-C sheet anodes (Figure 106d). The charge capacity was 1494 mAh g⁻¹ after 45 cycles with a capacity retention of over 94%. The CE for each cycle was stabilized above 98%. The rate capability of CNT-Si-C sheet was also measured under different current densities (50, 100, 200, 400 and 800 mA/g) (Figure 106e). Capacities maintained at around 1720, 1600, 1500, 1250, 1000 mAh g⁻¹ under each current density with a slight decrease in CE as the current density increased. The capacity returned to 1350 mAh g⁻¹ under a small current density (50 mA g⁻¹) after
undergoing charging cycles at 800 mA g$^{-1}$, indicating a good rate capability of the CNT-Si-C sheet anodes.

Figure 108. Morphologies after electrochemical cycling. SEM images of CNT-Si and CNT-Si-C sheets in the delithiated state after 20 cycles. CNT-Si sheets with different magnifications (a-c); CNT-Si-C sheet with different magnifications (d-f); Schematic of deformation of CNT-Si-C during lithiation and delithiation process (g).
SEM was used to investigate the morphological changes in the sheet anode structure in the fully delithiated state after 20 cycles. The CNT-Si sheet anode's morphology after cycling was very similar to that before cycling (Figure 108a). The silicon coatings were well intact without peeling off or detaching from tubes, but many cracks and fractures appeared in the silicon coating. Predictions of the radial, axial and hoop stresses developed in silicon coated cylindrical structures have been used to explain crack formation in the silicon coatings.\textsuperscript{68,69,152} Wang C. et al. recently demonstrated that an amorphous silicon layer had very strong adhesion on carbon nanofiber surfaces and that the thin silicon coating layer swelled/shrank only along the radial direction.\textsuperscript{69} Wang J. et al. found that cracks in the silicon were oriented along the carbon nanofiber axis and were attributed to the hoop stresses generated.\textsuperscript{152} However, their calculations showed that the magnitude of the axial stress was larger than that of hoop stress, contradicting their experimental results.\textsuperscript{152} In our case, cracks are found perpendicular to the axial direction, which is supported by their theoretical predictions that axial stress should be larger than that of the hoop stress (Figure 108b). Due to the strong adhesion between silicon and carbon, when cracks formed along the radial direction, the silicon shell remained well attached to the CNT, thus maintaining cyclic stability. As shown in the schematic in Figure 103g, the unique nano-grained silicon coating may contain some free space between grains. This structure may help to alleviate the internal stresses in the silicon coating during lithiation, reducing the amount of cracking and silicon separating from the surface of the CNT. Compared with the straight and aligned CNT-Si sheet anode in Figure 108b, the CNT-Si-C structure presented a waving structure after electrochemical cycling (Figure 108d). The question that remained is why did the CNT-Si sheet and CNT-Si-C sheet have different morphologies after
cycling? One possible explanation can be due to the confinement of the carbon coating, which will lead to the deformation of Si being accommodated preferentially along the axel direction of the CNT. Therefore in the charged state, the CNT is under tension, when discharged, it will be relaxed to form the waving structure. The other reason is possibly related to the differences in silicon morphology for the CNT-Si-C sheet. With a larger fraction of the grains being crystalline in the CNT-Si-C sheet, there is a larger strain induced by the lithiation, which we suspect is the main cause for the waving morphology. The number of large cracks across the individual coated tubes decreased (Figure 108e). This could be attributed to the deformation of the CNT and possibly the free space available between adjacent large silicon crystallites, which mitigated the mechanical strain and stress caused by the anisotropic expansion of Si crystals. The proposed deformation process of the CNT-Si-C sheet anode is shown in Figure 108g. It is thought that the Si coatings expanded, accompanied by SEI formation on newly-formed cracks and carbon surfaces. The maximum expansion state was achieved when the first deep lithiation process was complete. The following delithiation process would decrease the volume of Li-Si alloys and the compressive stresses during the contraction would be transferred to the CNT, causing them to buckle. Unlike randomly oriented CNT structures, the alignment in our structure allowed the silicon coated CNTs to buckle in phase. In the subsequent lithiation cycle, the accumulated stress was released and volume expansion straightened the CNTs again. The repeatable deformations of CNT-Si-C sheet under the electrochemical conditions allow us to hypothesize that a wave-like deformation can mitigate the strain and stress induced by the large volume change of the crystalline silicon, thus help to preserve the silicon and maintain structural stability of these
novel anode nanostructures. Our future work will focus on the influence of buckling behavior on the structural stability and electrochemical properties of electrode by introducing *in situ* techniques to observe the structural evolution and failure mechanism of CNT sheet composite in the long term cycling.

### 6.4 Conclusions

In summary, we designed novel, binder-free, thin sheet anodes for LIBs using aligned CNT-based silicon films which were processed in a way that is conducive to future commercial production. The horizontal super-aligned CNT sheets provides high surface area and a porous structure to facilitate the electrochemical kinetics between the silicon and the electrolyte. The CNT-based silicon composite sheet proved to have both high specific energy capacity and stable cycle performance. This work also revealed an interesting new mechanism of deformation for silicon coated CNT structures after electrochemical cycling. The spring-like deformation behavior of the aligned CNTs helped to explain the electrochemical stability of the crystalline silicon coatings. These findings will guide future work to optimize this unique nano-architecture for further increases in energy density and stability. This aligned CNT scaffold design will be extended to other anode and cathode materials utilized in thin and flexible LIBs.
CHAPTER 7 SULFUR GRADIENT-DISTRIBUTED CNF COMPOSITE: A SELF-INHIBITING CATHODE FOR BINDER-FREE LITHIUM-SULFUR BATTERIES

7.1 Introduction

In the pursuit of high electrochemical energy storage materials, significant efforts have been placed on exploring new types of battery chemistries and structures that have a combination of high energy density, improved safety, and reduced cost. Lithium-sulfur batteries are promising electrochemical power sources for various applications, including plugin electric vehicles (PEVs), due to their high energy density, large capacity, safe operating voltage, and potential for low cost production. Sulfur has a theoretical capacity of 1675 mAh g⁻¹, which is one order of magnitude greater than that of conventional cathode materials (e.g., LiCoO₂, LiFePO₄, and LiMn₂O₄) used in lithium-ion batteries. Therefore, even with a lower voltage of 2.2 V vs. Li/Li⁺, the theoretical specific energy of a lithium-sulfur cell is about 2500 Wh kg⁻¹, which is five times greater than that of a graphite/LiCoO₂ cell. However, the study of lithium-sulfur batteries faces several challenges, including low sulfur utilization, low coulombic efficiency and rapid capacity loss during repeated cycling. These problems are caused by the low electronic conductivity of sulfur and its discharge products, and the diffusion, shuttling effect, and side reactions of soluble polysulfides produced during electrode reactions. Figure 109a shows the diffusion and shuttling of polysulfides in the electrolyte between a normal sulfur cathode and a lithium metal anode, and also the resultant deposition of insoluble Li₂S on the anode due to side reactions between dissolved polysulfides with lithium.
The most commonly studied approach to solve these problems is to make sulfur-carbon composites. Many sulfur-carbon composites not only have increased electrical conductivity, but also store the active material inside the carbon matrix. Representative work has been reported by Nazar and co-workers on a highly ordered mesoporous carbon-sulfur composite structure. Sulfur was embedded into the pores of CMK-3 mesoporous carbon where the reduction/oxidation reactions of sulfur took place locally and the polysulfides could be captured by the high surface area of carbon. The resultant cathode delivered a stable capacity over 1000 mAh g⁻¹ after 20 cycles. This work provided an effective way to achieve high sulfur utilization, inspiring researchers to design different types of nanostructures with high surface area to encapsulate sulfur for cathode materials. However, most sulfur-carbon nanocomposites have low tap densities and the synthesis methods, including carbon preparation and sulfur impregnation, are typically complicated and high cost, which limits their possible use in lithium-sulfur batteries. Recently, Manthiram’s group developed a novel dual-layer sulfur cathode by placing a microporous carbon paper as an interlayer between a normal sulfur cathode and a separator to capture the migrating polysulfides from the cathode during electrochemical reactions, and a significant improvement was achieved in the sulfur utilization and capacity retention. Figure 109b shows the schematic configuration of a lithium-sulfur cell with the dual-layer sulfur cathode, which was developed by Manthiram’s group. The carbon interlayer can not only reduce the interfacial resistance in the cathode but also prevent polysulfides from migrating to the anode. In addition to the microporous carbon paper, other carbon structures such as carbon nanotube paper, treated carbon paper, carbonized Kimwipes have also been used to prepare the dual-layer sulfur cathodes and the resulting
electrochemical performance was promising in all of those cases. As a result, multiple layers and large mass of carbon papers are required to achieve good sulfur performance. However, one challenge of this dual-layer configuration is the relative lower sulfur content if the weight of the entire electrode including the carbon interlayer is taken into consideration. The carbon interlayer decreases the specific capacity of cathode and reduces the overall energy density of a lithium-sulfur cell, which makes the goal of replacing lithium-ion batteries more challenging. Therefore, it is important to obtain a cathode that can simultaneously have high sulfur loading/content and good electrochemical performance.

To address this challenge, a new lithium-sulfur configuration using a self-inhibiting, gradient sulfur composite cathode is presented in this communication and is shown schematically in Figure 109c. Polysulfides created during electrochemical reactions will be retained within the cathode region to minimize the effects of polysulfide shuttling as well as side reactions on the lithium metal anode. This sulfur composite is mechanical flexible and highly electrically conductive with its integral structure serving all important functions in the cathode simultaneously. It can work as a binder-free electrode in lithium-sulfur cells without need of polymer binder or Al foil. The elimination of these non-active components will significantly reduce the weight burden and as a result, the overall battery capacity will be increased dramatically. More importantly, the sulfur composite has a gradient sulfur distribution along the composite’s thickness which forms a high-sulfur, a low-sulfur, and a non-sulfur region (Figure 109d), which function together as a polysulfide-inhibitor. The high-sulfur region is a sulfur resource that functions as sulfur electrode while the nano-carbon supporting network
decreases the internal charge transfer resistance. The low-sulfur region operates as a reservoir to localize the dissolved polysulfide and the non-sulfur region acts as an inhibitor to prevent polysulfide migration between electrodes. In the battery, the three regions work synergistically to provide high conductivity and inhibit the polysulfides from leaving the cathode structure to achieve high sulfur utilization and good cycling stability. As a result, this new self-inhibiting, gradient sulfur cathode structure can address the challenges faced by conventional sulfur cathodes and outperform dual-layer cathodes when the mass of the carbon component is taken into account in the specific capacity.

Figure 109. (a-c) Schematic configuration of a lithium-sulfur cell with a sulfur cathode, a dual-layer sulfur cathode, and a self-inhibiting, gradient sulfur cathode, respectively. (d) Schematic of the self-inhibiting, gradient sulfur cathode with high-sulfur region, low-sulfur-region, and non-sulfur region. (e) Schematic of the synthesis process of the carbon nanofiber-sulfur (CNF-S) composite. Elemental sulfur was vaporized in a furnace and the sulfur vapor was protected by argon and transported to the deposition zone, where the CNF web was placed.
7.2 Experimental

7.2.1 Material Synthesis & Electrode Preparation

CNF webs were prepared by electrospinning polyacrylonitrile (PAN) (Mw: 150,000 g mol⁻¹), followed with carbonization. Details of the CNF preparation process was reported in earlier work. CNF webs have a density of 1.5 - 1.8 mg cm⁻² with a thickness of around 0.15 mm. To produce the CNF-S composites, sulfur was deposited onto CNF webs directly by a chemical vapor deposition system operating at different temperatures (250, 300, and 350 °C). The schematic of the sulfur deposition process is shown in Figure 1a. 100mg elemental sulfur (99.5-100.5% Sigma-Aldrich) was placed at the center of the tube furnace, with the CNF substrates loaded downstream at a distance of 20cm away from the center of the chamber. During the deposition process, the chamber was heated up at a rate of 30 °C/min under a 20 sccm flow of Ar gas, held at the set point temperature for 15 min, and then cooled down to room temperature naturally. In this work, the actual sulfur loading density of CNF-S (250 °C), CNF-S (300 °C), and CNF-S (350 °C) composites were 0.5, 1.7, and 2.6 mg cm⁻², respectively. Conventional sulfur cathode was fabricated by mixing 70 wt% of elemental sulfur, 20 wt% of carbon black, and 10 wt% of polyvinylidene fluoride binder in an N-methylpyrrolidinone (Sigma-Aldrich) solution. The slurry was casted onto an aluminum foil and dried in a vacuum oven overnight at 60 °C, followed by cutting into circular electrodes. The sulfur loading was ~2.0 mg cm⁻².

7.2.2 Characterization

The morphology of the CNF-S composites was investigated using a field emission scanning electron microscope (FE-SEM, JEOL 6400F). The crystallographic and chemical structures
were studied using wide angle X-ray diffraction (WAXD, Rigaku Smartlab) and a Renishaw Raman microscope (514 nm). The water contact angles were measured with a goniometer (model 290-F4 Ramé-Hart, Ramé-Hart Inc., Succasunna, NJ) by capturing the image of droplet using DROPImage software. The volume of the deposited water droplets was 2 μL.

**7.2.3 Electrochemical Evaluation**

CNF-S composites were used directly as the cathode electrode for lithium-sulfur batteries. All the cathode disks and CNF interlayer were dried in a vacuum oven overnight at 60 °C before assembling the cell. Lithium ribbon (99.9%, Aldrich) was used as the counter electrode and Celgard 2400 membrane as the separator. The electrolyte was prepared by dissolving 1.0 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and 0.1 M lithium nitrate in a 1:1 volume ratio of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME). The amount of electrolyte was added according to the actual mass of sulfur in the cathode electrode, with an electrolyte/sulfur ratio of around 10 mL g⁻¹. In each cell, the mass of sulfur in CNF-S (250 °C), CNF-S (300 °C), and CNF-S (350 °C) was around 0.6 mg, 2.2 mg, and 3.3 mg, respectively. The 2032 coin cells were assembled in an argon-filled glove box. All cells were allowed to rest for 3 hours at room temperature before electrochemical measurements. Cyclic voltammetry (CV) measurements were performed by using a Gamry reference 600 Potentiostat/Galvanostat/ZRA device at a scan rate of 0.05 mV s⁻¹ in a potential range of 1.5-3.0 V. The discharge-charge voltage curves and cycling tests were carried out on a LAND-CT 2001A battery test system with cut-off potentials between 1.5 and 3.0 V. The electrochemical impedance spectra (EIS) were obtained on Gamry reference 600 by scanning cells between 1 MHz and 100 MHz at room temperature.
7.3 Results and Discussions

This self-inhibiting, gradient sulfur composite was synthesized by depositing sulfur vapor on a carbon nanofiber (CNF) sheet in a sulfur vapor deposition furnace. The schematic synthesis of the CNF-S composite is shown in Figure 1e. As the elemental sulfur was melted in a furnace, the sulfur vapor was transported along a tunnel to deposit on the CNF sheet to get the CNF-S composite. With control of the furnace temperature, sulfur deposition time and feeding rate, the structure of the CNF-S composites can be manipulated correspondingly. This sulfur vapor deposition provides a simple, continuous, and economical strategy to produce cathodes at high speed and low cost. In this work, the furnace temperature was controlled at 250, 300, and 350 °C to produce sulfur vapor and obtain CNF-S composites.

The top view of the CNF-S composites prepared at furnace temperatures of 300 and 350 °C shows a dense sulfur coating on the CNF sheet surfaces, as shown in Figure 110a-b. The CNF-S prepared at furnace temperature of 250 °C exhibited a totally different surface morphology that consisted of a light sulfur coating on the individual CNFs instead of covering the whole sheet surface. At the higher furnace temperatures, dense sulfur coating was formed on the surface, demonstrating the morphology we proposed in Figure 109d. In the CNF-S (300 °C) composite, a high-sulfur region was formed with a rough plateau topology where regions of thicker sulfur deposition make up the sulfur plateaus and some of uncoated individual CNFs were only lightly coated on the surface (Figure 110c). Empty space was left around those sulfur plateaus and formed macroporous channels to facilitate the penetration of electrolyte into the internal space of the CNF-S composite. In the CNF-S (350 °C) composite, the entire
CNF sheet was covered by sulfur and the sulfur coating appears denser than that in the CNF-S (300 °C) composite (Figure 110d). Most of the sulfur plateaus were linked together, leaving only a few macroporous channels on surface. Of the three samples, the CNF-S (350 °C) composite exhibited the smoothest surface on the sulfur coated side. To confirm the gradient sulfur distribution through the thickness of composite, composites were cut in the cross-sectional direction. This sulfur gradient can be discerned clearly in Figure 110e-f. The outer layer of the CNF-S (350 °C) composite is the high-sulfur region, having a thickness of ~4 μm. It was found that a 3-dimentional porous structure was formed within the CNF space. The middle of the structure had a much smaller pore size than in the non-sulfur region. This porous sulfur network exhibited a relative lower sulfur density than the outer dense sulfur coating and was the low-sulfur region. The low-sulfur region had a thickness of ~12 μm, which is around two times thicker than the low-sulfur region in the CNF-S (300 °C) composite, indicating that a higher furnace temperature facilitated a deeper sulfur penetration within the CNF sheet. The three defined regions, confirmed the successful synthesis of the proposed gradient CNF-S structure.
Figure 110. Morphologies of CNF-S composites. (a,c) SEM images of the top view of the CNF-S (300°C) composite. (b,d) SEM images of the top view of the CNF-S (350°C) composite. (e,f) SEM images of the side view of the CNF-S (300°C) composite and the CNF-S (350°C) composite, respectively.
To confirm the gradient CNF-S structure, Raman spectroscopy was applied to detect sulfur signals on both sides of the CNF-S (350 °C) composite. The three high-intensity peaks (centered at 155, 220, and 475 cm$^{-1}$, respectively) in the Raman spectrum of the sulfur side of the CNF-S structure (Figure 111a) correspond to the characteristics signals of the S$_8$ molecule. The same sulfur spectra was not detected on the other side (i.e., the non-sulfur region) of the composite, confirming the gradient sulfur distribution along the cross-section of the CNF web. X-ray diffraction (XRD) patterns of elemental sulfur, CNF sheet, and CNF-S composites prepared at different temperatures are shown in Figure 111b. In the spectrum of elemental sulfur, the largest sulfur peaks fell mainly within the 20-30 degree range. The CNF-S composite showed strong sulfur peaks in the same two theta range as elemental sulfur, indicating that a large amount of sulfur remained on the composite surface instead of being embedded inside the carbon structure. This result is different from others’ work in which sulfur is encapsulated within carbon porous structures. To demonstrate the high electrolyte and polysulfide uptake by the CNF-S structure, Figure 111c-d show liquid retention test of a CNF sheet and contact angle measurements of both the non-sulfur side and the sulfur side of CNF-S composites, respectively. All the tested materials were the same size as the electrodes used for coin cells. For the safety reasons, deionized water was used instead of electrolyte for these tests. In the liquid retention test, deionized water with a volume of 0.23 mL was maintained in a CNF disk. The super liquid absorbency further indicates that the CNF sheet can work as a reservoir to self-inhibit polysulfides by localizing liquid electrolyte and the polysulfides. Surface contact angle results confirm that the non-sulfur region of CNF-S composites have a superior liquid absorbency that can allow liquid to penetrate into the overall electrode structure.
fast and easily. The contact angle decreased from 111 degrees of the CNF-S (250 °C) to 87 degrees of the CNF-S (350 °C), indicating an improved wetting property of the sulfur-region in CNF-S composite. The decrease of the contact angle was a result of the change in the coating roughness and the hydrophobic nature of sulfur. The improved wetting properties of the sulfur side was favorable for electrolyte absorption. Since the low-sulfur region has a porous sulfur network with smaller pore size, the liquid can be pulled by capillary force from the non-sulfur region and high-sulfur region into the low-sulfur regions. If both sides were sulfur coated then wetting of the overall electrode might be more challenging. Therefore, the gradient CNF-S structure played an important role in self-inhibiting polysulfide and retaining electrolyte within cathode.
Figure 111. Structural characterizations of CNF-S composites. (a) Raman spectra of top and bottom sides of CNF-S (350°C) composite. Sulfur peaks indicate that sulfur was mainly deposited on the top side, not the bottom side of the CNF web. (b) XRD spectra of elemental sulfur, CNF web, and CNF-S composites. Sharp sulfur peaks indicates that sulfur was coated on CNF surfaces rather than diffused into individual CNFs. (c) Photo image of water-absorbed CNF web. CNF shows a high absorbency of water. (d) Surface contact angle measurements of CNF-S composites. Non-sulfur side and high-sulfur side shows different wetting behavior.

Electrochemical characterizations were conducted to demonstrate the polysulfide self-inhibiting function of the CNF-S composite. Cyclic voltammetry (CV) plots of the CNF-S (350°C) composite, in the first three cycles, are shown in Figure 112a. CV measurements were performed at a scan rate of 0.05 mV s⁻¹ in a potential range of 3.0-1.5 V. Typically, elemental
sulfur features two reduction current peaks at ~2.3 V and ~2.0 V in liquid electrolyte, corresponding to a solid-to-liquid (from S_8 to dissolved Li_2S_8) phase transition and a liquid-to-solid (from the dissolved Li_2S_6 to Li_2S_2/Li_2S) phase transition, respectively. The CNF-S (350 °C) composite exhibited only one reduction peak with a large current density at 1.85 V in the first cycle, which is different from the two-step sulfur reduction process. This single and broad reduction peak suggests a solid-to-solid phase transition, which is due to the over-potential caused by the poorly conducting interface between heavily loaded sulfur and CNF. The anodic peak at 2.6 V results from the oxidation reaction from low-order polysulfides to S_8/Li_2S_8. The large separation between cathodic and anodic peaks implies high polarization in the first cycle. In the following two cycles, two reduction peaks appear at 2.3 and 2.0 V, respectively, indicating the presence of normal solid-to-liquid and liquid-to-solid phase-change reactions. The overlap of peaks with smaller separations at the 2nd and 3rd cycles implies that the CNF-S composite has superior cycle stability and highly reversible redox reactions.

Impedance analysis conducted on the CNF-S (350 °C) composite confirmed that this novel electrode configuration has higher conductivity than the conventional sulfur cathode, even when the former one has a much higher sulfur loading density (Figure 112b). The electrolyte resistance (intersection of the high-frequency portion of the semi-circle with the real axis) for the conventional sulfur cathode was 15.9 ohm while the CNF-S (350 °C) composite was only 2.4 ohm. In addition, the impedance of the CNF-S composite continuously decreased in the first three cycles, and this decrease was possibility due to the redistribution of sulfur within the CNF web, which was favorable to the improvement of the CNF-S electrochemical
properties. Figure 4b also shows that the electrolyte resistance remained constant during the first few cycles with the CNF-S composite, indicating that no polysulfide traveled out of the CNF structure or migrate between the two electrodes.

The initial (Figure 112c) and subsequent discharge-charge (Figure 112d) curves correlated well with the CV curves (Figure 4a) for the CNF-S (350 °C) composite. A sloping voltage plateau starting at 2.1 V with a significant voltage hysteresis and a much larger discharge capacity for the initial discharge of CNF-S (350 °C) is apparent in Figure 4c. In the following 10 cycles, as shown in Figure 112d, the prolonged low voltage plateau and decreased voltage difference between discharge and charge curves showed that more sulfur was activated and participated in the reduction reaction, indicating that sulfur was rearranged to favorable electrochemical positions in the CNF web.\(^9\) The initial discharge-charge curves of the conventional sulfur cathode and the CNF-S cathodes prepared at different temperatures are shown in Figure 112c. The conventional sulfur cathode had a sulfur loading density of 2.0 mg cm\(^{-2}\). For comparison, a dual-layer sulfur cathode was also prepared and tested. In the dual-layer cathode, a CNF web was placed between the separator and the conventional sulfur cathode, functioning as an interlayer to trap polysulfide and enhance cathode conductivity.\(^9\) As shown in Figure 112c, the conventional sulfur cathode delivered a discharge capacity at 613.3 mAh g\(^{-1}\), indicating that only 36.6% sulfur was utilized. For the dual-layer sulfur cathode, the discharge capacity increased to 967.4 mAh g\(^{-1}\), corresponding to an increased efficiency of 57.8% in the sulfur utilization. The increased discharge capacity demonstrated the positive effect of introducing a carbon interlayer into the battery configuration.\(^9\) For CNF-
S composites, specific capacity varied with increasing sulfur loading. The CNF-S (250 °C) composite had the smallest sulfur content and sulfur loading at 19.2% and 0.51 mg cm\(^{-2}\), respectively. Its initial discharge capacity reached 1681.3 mAh g\(^{-1}\), which is slightly higher than the theoretical capacity (1675 mAh g\(^{-1}\)) of sulfur, indicating a high sulfur utilization. The CNF-S (300 °C) and CNF-S (350 °C) composites reported here had a sulfur loading at 1.6 and 2.6 mg cm\(^{-2}\), and a sulfur content at 42.0% and 64.6%, respectively. They delivered an initial discharge capacity at 1267 and 1026 mAh g\(^{-1}\), respectively. The reduction plateau below 1.8 V became much smaller in the CNF-S (300 °C) and CNF-S (350 °C) composites and disappeared in the following cycles (Figure 112d), indicating that once sufficient Li\(_2\)S\(_2\)/Li\(_2\)S from the extended-released sulfur occupied the free CNF surface before 1.8V, the continuous consumption of the reduced LiNO\(_3\) process might be terminated. Figure 112d also shows that the CNF-S (350 °C) composite had a decreased polarization and retained a very stable capacity from the 50\(^{th}\) cycle to 100\(^{th}\) cycle.

In the cycling performance tests (Figure 112e), the dual-layer sulfur cathode exhibited higher discharge capacity (500 mAh g\(^{-1}\)) and better cyclability than the conventional sulfur cathode (<200 mAh g\(^{-1}\)). This was attributed to the fact that the CNF sheet works both as a current collector to improve the active material utilization and a polysulfide sink to trap the dissolved polysulfide.\(^1\)\(^{98}\) Based on the mass of sulfur, the CNF-S (250 °C) composite showed high initial discharge capacity, however, the capacity declined during cycling because polysulfide dissolved into electrolyte and diffused out of CNF web due to the low concentration of the dissolved polysulfide in the electrolyte which had a low viscosity,\(^1\)\(^{73}\) thus higher sulfur content.
in the CNF-S composite results in high viscosity with a high concentration of the dissolved polysulfides so as to prevent them diffusing out of CNF sheet. The CNF-S (300 °C) composite had the highest capacity value of around 1000 mAh g\(^{-1}\) and highest capacity retention of around 95% at 50\(^{th}\) cycle. The CNF-S (350 °C) composite showed gradual capacity increases during the first 10 cycles and slight decreases in the next 15 cycles, and then remained at a stable capacity of 700 mAh g\(^{-1}\) in the subsequent cycles. These results indicate that among all samples studied, the CNF-S (300 °C) composite had the best electrochemical performance.

So far, most researchers have focused on improving the capacity and cycling life of sulfur cathodes.\(^{173,174}\) The capacity values in most literature reports have been calculated based solely on the mass of sulfur. However, if a sulfur cathode has low sulfur loading or sulfur content, the high capacity calculated based on sulfur may not reflect the true electrochemical performance of the cathode due to the presence of a large amount of inactive materials such as polymer binder, carbon black, and Al foil. Our CNF-S composites have high sulfur loading and high sulfur content, and they can be used directly used as sulfur cathodes in practical lithium-sulfur batteries without the use of polymer binder, carbon black, and Al foil. Hence, the high capacities and good cycling performance of the CNF-S composites will directly result in good electrochemical performance of the batteries. Figure 112f compared the capacities and cycling performance of CNF-S composites with those of conventional and dual-layer sulfur cathodes by normalizing the capacities based on the total mass of the electrode configuration including the carbon interlayer. It is seen that CNF-S (300 °C) and CNF-S (350 °C) composites always exhibited significantly higher capacities than other cathodes during cycling. The capacity of 400 mAh g\(^{-1}\) is considered
to be the lithium-ion cell equivalent as typical cathodes in lithium-ion batteries deliver around 200 mAh g$^{-1}$ capacity but with higher operating voltage (~4 V) than lithium-sulfur batteries.$^{174}$ Note that since the CNF-S (350 °C) composite had high sulfur loading (2.6 mg cm$^{-2}$) and high sulfur content (~65%), the cycling results are very promising and this novel CNF-S electrode design shows great potential as one high-capacity cathode candidate for increasing the total energy density of lithium-sulfur cells.
**Figure 112.** Electrochemical properties of CNF-S composites. (a) Cyclic voltammetry profiles of CNF-S (350°C) at a scan rate of 0.05 mV s⁻¹ between 3.0 V and 1.5 V. (b) Electrochemical impedance spectroscopy plots of CNF-S (350°C) and conventional sulfur electrode. (c) Initial discharge-charge curves of conventional sulfur electrode, CNF-inserted dual-layer sulfur electrode, and CNF-S composites at 100 mA g⁻¹. (d) Discharge-charge curves of CNF-S (350°C) at 100 mA g⁻¹. (e) Cycling performance of conventional sulfur electrode, CNF-inserted dual-layer sulfur electrode, and CNF-S composites at 100 mA g⁻¹. The capacity is based on sulfur mass only. (f) Cycling performance of conventional sulfur electrode, CNF-inserted dual-layer sulfur electrode, and CNF-S composites at 100 mA g⁻¹. The capacity is normalized to the total weight of electrode.
To investigate the structural change in the sulfur coating after cycling, the CNF-S (350 °C) composite was examined in a fully charged state after charge-discharge cycling. Disassembly of the cell was carried out in an argon-filled glove box and the composite cathode was washed in 1,3-dioxolane (DOL)/dimethoxy ethane (DME) solution and dried before SEM observation. Figure 113 gives the SEM images of the CNF-S (350 °C) composite after 200 cycles. The insets are the corresponding photographs of two sides of the CNF-S composite. As shown in Figure 113a-b, the smooth sulfur coating in the high-sulfur region disappeared, leaving a rough and porous sulfur morphology. The agglomerated sulfur is trapped by CNFs. In the non-sulfur region of the CNF-S composite, a small amount of sulfur is collected on the surface of the CNFs (Figure 113c-d). The trapped sulfur in the high-sulfur region and the small amount of sulfur in the non-sulfur region indicate that the hierarchical structure of the CNF-S composite can help reduce the diffusion of polysulfide out of the non-sulfur region by blocking the dissolved polysulfide transportation.
7.4 Conclusions

In summary, we have developed a multifunctional CNF-S composite with high sulfur loading (~2.6 mg cm\(^{-2}\)) and high sulfur content (~65%) as a promising binder-free and Al-free cathode (~2.1 mAh cm\(^{-2}\)) for high-energy lithium-sulfur batteries. This CNF-S composite has a unique structure with a gradient sulfur distribution that consists of a high-sulfur region, low-sulfur...
region, and non-sulfur region through the thickness of CNF web. The CNF-S composite not only has high sulfur loading but also helps to localize the dissolved sulfur and polysulfide. In addition, a novel sulfur vapor deposition strategy was demonstrated and proved to be an effective way to synthesize the carbon-sulfur cathodes, which greatly shortens the composite preparation time, especially the sulfur loading time, from tens of hours to a few minutes. This advanced electrode structure with extremely high capacity and superior stability is a promising cathode candidate to replace the normal sulfur electrode and cell configuration for lithium-sulfur batteries in the near future.
CHAPTER 8 RECOMMENDATION WORK

The importance of confined silicon structure to the improvement in electrochemical performance of silicon electrode composites has been studied and discussed in the previous chapters. To further address challenges met in the experiments, the following future work is recommended:

For the carbon nanofiber projects, the confinement of silicon by coating carbon and creating empty chamber proved to be two effective strategies to overcome some aspects of challenges faced by silicon and its composites. It is found that mechanical enhancement in carbon structure and SEI control on silicon surface are the two key factors that determine the capacity and cycling life of silicon electrode materials. Although empty chamber could accommodate the volume change of silicon nanoparticles, the continuously growth of SEI on silicon surfaces would inevitably take up the whole empty chamber and eventually break the carbon matrix. To find an effective way to control the SEI formation on surfaces of embedded silicon nanoparticles becomes one major objective in the future work. According to the results obtained in this dissertation work, CVD amorphous carbon could stabilize SEI and enhance mechanical confinement of silicon. A recommended future project is to conformally coat this bi-functional carbon on both silicon nanoparticles and their carbon nanofiber out layers. The CVD amorphous carbon on silicon particles is used to block the direct contact between silicon nanoparticles and the electrolyte and at the same time buffer the silicon volume expansion. The outer CVD amorphous carbon coating on carbon nanofiber surface is used to enhance the
mechanical confinement of silicon within carbon matrix. The mechanical properties of CVD-produced carbon and PAN-derived carbon can be studied and compared, and properties behind the two different carbon structures will give us a better understanding of the relationship between carbon and silicon in the process of silicon volume change behaviors.

For the carbon nanotube project, conformal carbon coating has demonstrated good mechanical constraint to the silicon and its electrochemical performance exhibited a significant improvement compared to the one without carbon coating. In this dissertation work, a deformation along the longitudinal direction of carbon nanotube was observed for the conformal carbon coated sample. The super-aligned carbon nanotube maintained intact with few cracks on the coatings. The intact morphology and wave-like deformation arouse the interest to \textit{in-situ} observe the complete deformation process in the electrochemical environment. Thus, a recommended future project is to cooperate with Pacific Northwest National laboratory to explore the mechanism behind the conformal carbon coated silicon-carbon nanotube structures.

For lithium-sulfur batteries, we developed a facile and fast method to load sulfur onto carbon materials. In this dissertation work, self-supported PAN-derived carbon nanofiber web was used directly as the carbon matrix to load sulfur onto surfaces. This sulfur-carbon nanofiber composite had high sulfur content and sulfur loading and the resultant high capacity made it a promising binder-free and current collector-free cathode materials. Besides by using carbon nanofibers, carbon nanotubes were also introduced to this cathode design. Carbon nanotubes
are believed to have the capability of trapping more dissolved polysulfide due to the high specific surface area. However, fast capacity decay was observed and we attribute it to the poor mechanical property of the super-aligned carbon nanotube structure with the comparison of strong inter-twined carbon nanofiber web. Therefore, one recommended future project is to introduce a carbon nanofiber-carbon nanotube (CNF-CNT) inter-connected nonwoven structure into sulfur cathodes. This structure can be achieved by directly electrospun PAN nanofiber onto the drum-collected carbon nanotube sheet and followed with carbonization process. This CNF-CNT structure is believed to exhibit good mechanical support and high surface area, which is an ideal carbon structure to be applied with our newly designed sulfur loading method for sulfur cathode.

In addition to the abovementioned electrode work, full cells can be prepared by using our newly developed sulfur cathode and lithiated silicon anode. A flexible full battery can be designed and developed by using these cathodes and anodes incorporated with electrospun nanofiber based separators.
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