DEVELOPMENT OF HIGH-ENERGY SILICON-BASED ANODE MATERIALS
FOR LITHIUM-ION STORAGE

A Dissertation in
Mechanical Engineering
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2015
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ABSTRACT

The emerging markets of electric vehicles (EV) and hybrid electric vehicles (HEV) generate a tremendous demand for low-cost lithium-ion batteries (LIBs) with high energy and power densities, and long cycling life. The development of such LIBs requires development of low cost, high-energy-density cathode and anode materials. Conventional anode materials in commercial LIBs are primarily synthetic graphite-based materials with a capacity of ~370 mAh/g. Improvements in anode performance, particularly in anode capacity, are essential to achieving high energy densities in LIBs for EV and HEV applications.

This dissertation focuses on development of micro-sized silicon-carbon (Si-C) composites as anode materials for high energy and power densities LIBs. First, a new, low-cost, large-scale approach was developed to prepare a micro-sized Si-C composite with excellent performance as an anode material for LIBs. The composite shows a reversible capacity of 1459 mAh/g after 200 cycles at 1 A/g (97.8% capacity retention) and excellent high rate performance of 700 mAh/g at 12.8 A/g, and also has a high tap density of 0.78 g/cm³. The structure of the composite, micro-sized as a whole, features the interconnected nanoscale size of the Si building blocks and the uniform carbon filling, which enables the maximum utilization of silicon even when the micro-sized particles break into small pieces upon cycling.

To understand the effects of key parameters in designing the micro-sized Si-C composites on their electrochemical performance and explore how to optimize them, the influence of Si nanoscale building block size and carbon coating on the electrochemical performance of the micro-sized Si-C composites were investigated. It has been found that the critical Si building block size is 15 nm, which enables a high capacity without compromising the cycling stability, and that carbon coating at higher temperature improves the 1st cycle coulombic efficiency (CE) and the rate capability. Corresponding reasons underneath electrochemical performance have been revealed by various characterizations. Combining both optimized Si building block size and carbon coating temperature, the resultant composite can sustain 600 cycles at 1.2 A/g
with a fixed lithiation capacity of 1200 mAh/g, the best cycling performance with such a high capacity for micro-sized Si-based anodes.

To further improve the rate capability of Si-based anode materials, an effective method of facile boron doping was demonstrated. Boron-doped Si-C composite can deliver a high capacity of 575 mAh/g at 6.4 A/g without addition of any conductive additives, 80% higher than that of undoped composite. Compared to the obvious capacity fading of undoped Si-C composite, boron-doped Si-C composite maintains its capacity well upon long cycling at a high current density. Electrochemical impedance spectroscopy (EIS) measurement shows boron-doped Si-C composite has lower charge transfer resistance, which helps improve its rate capability.

A novel micro-sized graphene/Si-C composite (G/Si-C) was then developed to translate the performance of such micro-sized Si-C composites from the material level to the electrode level aiming to achieve high areal capacities (mAh/cm²) besides gravimetric capacities (mAh/g). Owing to dual conductive networks both within single particles formed by carbon and between different particles formed by graphene, low electrical resistance can be maintained at high mass loading, which enables a high degree of material utilization. Areal capacity thus increases almost linearly with mass loading. As a result, G/Si-C exhibits a high areal capacity of 3.2 mAh/cm² after 100 cycles with high coulombic efficiency (average 99.51% from 2nd to 100th cycle), comparable to that of commercial anodes.

Finally, a micro-sized Si-based material (B-Si/SiO₂/C) featuring high rate performance was developed via a facile route without use of toxic hydrofluoric acid. A Li-ion hybrid battery constructed of such a Si-based anode and a porous carbon cathode was demonstrated with both high power and energy densities. Boron-doping is employed to improve the rate capability of B-Si/SiO₂/C. At a high current density of 6.4 A/g, B-Si/SiO₂/C delivers a capacity of 685 mAh/g, 2.4 times that of the undoped Si/SiO₂/C. Benefiting from the high rate performance along with low working voltage, high capacity and good cycling stability of B-Si/SiO₂/C, the hybrid
battery exhibits a high energy density of 128 Wh/kg at 1229 W/kg. Even when power density increases to the level of a conventional supercapacitor (9704 W/kg), 89 Wh/kg can be obtained, the highest values of any hybrid battery to date. Long cycling life (capacity retention of 70% after 6000 cycles) and low self-discharge rate (voltage retention of 82% after 50 hours) are also achieved.
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ACKNOWLEDGMENTS

I would like to express my heartfelt appreciation and thanks to my advisor Professor Donghai Wang for his tremendous support and encouragement. His advice on my research has been priceless. I will never forget his hardworking attitude and passionate debates on research between us.

I sincerely thank my committee members Dr. Chris Rahn, Dr. Michael Hickner, Dr. Sulin Zhang and Dr. Ayyakkannu Manivannan for their time, efforts, and insightful comments.

I could not have written this dissertation without an amazing group of colleagues. Special thanks to Dr. Fang Dai, with whom I closely worked for two years on silicon-related projects, for his inspirations and kind help. I would like to thank my current colleagues for their collaborations and discussions: Mikhail Gordin, Shuru Chen, Zhaoxin Yu, Qingquan Huang, Michael Melnyk, Yue Gao, Dr. Jiangxuan Song, Dr. Duihai Tang and Dr. Shi Hu. Also I would like to acknowledge the past members in Dr. Donghai Wang’s group, including Dr. Zhiping Song, Dr. Zhongxue Chen, Dr. Da Chen, Dr. Dongping Lv, Dr. Jiantao Zai, Dr. Hiesang Sohn and Dr. Tianren Xu.

Finally, I am deeply indebted to my parents and my wife, who have supported me throughout entire process, for their understanding and endless love. I will be grateful forever for your love.
Chapter 1: Introduction to the Development of Silicon-based Anode Materials for Lithium-ion Batteries

1.1 Introduction to Lithium-ion Batteries

It is now almost universally recognized that gaseous emissions from the burning of fossil fuels are not only polluting the air of large, modern cities but are also creating a global warming with alarming consequences. The primary candidates as alternatives to fossil fuel are hydroelectric, nuclear, and renewable. These sources require energy storage. The most convenient form of energy storage is portable chemical energy and the battery provides the portability of stored chemical energy with the ability to deliver this energy as electrical energy with a high conversion efficiency and no gaseous exhaust.\(^1\) Among the various existing technologies, Li-based batteries, because of their high energy density and design flexibility (Figure 1), currently outperform other systems, accounting for 63% of worldwide sales values in portable batteries.\(^2\)

![Figure 1-1. Comparison of the different battery technologies in terms of volumetric and gravimetric energy density.\(^2\)](image)
Lithium ion battery stores energy by chemical reaction, the reaction mechanism is presented in Figure 2. Lithium ions move back and forth between the positive and negative electrode during charge and discharge. During discharging, the battery acts like a galvanic cell, converting chemical energy to electric energy. During charging, the battery acts like an electrolytic cell, which uses electricity to motivate a desired redox reaction. The main components of lithium ion batteries are cathodes, anodes, separator, and electrolyte. A cathode is the positive electrode which is reduced during discharge. While the anode which is also called negative electrode is oxidized. The separator allows lithium ion pass through but prevents electrodes from short circuit.

![Figure 1-2](image-url)  
**Figure 1-2.** A schematic illustration of the working principles of a Li$_x$C$_6$/ Li$_{1-x}$CoO$_2$ lithium-ion cell. During discharge, lithium ions diffuse from a lithiated graphite (Li$_x$C$_6$) structure (the anode) into a delithiated Li$_{1-x}$CoO$_2$ structure (the cathode) with concomitant oxidation and reduction of the two electrodes, respectively. The reverse process occurs during charge.\(^\text{[3]}\)

### 1.2 Challenges for Li-ion anode materials

The emerging markets of electric vehicles (EV) and plug-in hybrid electric
vehicles (PHEV) generate a tremendous demand for low-cost lithium-ion batteries (LIBs) with high energy and power densities, and long cycling life.[4-7] The development of such LIBs requires development of low cost, high-energy-density cathode and anode materials. Considering the use of current cathode materials with capacities of 200 mAh/g, and other cell components (electrolyte, separator, current collector, etc), development of anode materials having specific capacity on the order of 1200-1500 mAh/g can almost double the specific capacity of Li-ion full battery cells and thus the energy density for EV and PHEV applications (Figure 3).[8]

Conventional anode materials in commercial LIBs are primarily synthetic graphite-based materials with a capacity of ~370 mAh/g.[9] Improvements in anode performance, particularly in anode capacity, are essential to achieving high energy densities in LIBs for EV and PHEV applications.

![Figure 1-3. Effects of anode and cathode capacity on the overall battery capacity of rechargeable Li-ion batteries.][8]

1.3 Development of Silicon-based Anode Materials

Li alloys of group IV materials (Si, Ge and Sn) have attracted increasing attention as potential high-capacity anode materials owing to their abilities to uptake 4.4 lithium atoms per atom. Among the metal that can react with lithium, silicon is the most promising candidate for next generation lithium-ion battery anode materials.
Upon lithiation, when the silicon active material is transformed from a crystalline structure to a metastable amorphous/crystalline structure, a single silicon atom can accommodate approximately 4 lithium atoms (i.e. Li$_{4.4}$Si)\textsuperscript{[10]}. Therefore, one of the desirable aspects of silicon is its high theoretical specific capacity (ca. 4200 mAh/g) and safety characteristics. Furthermore, the 0.4 V onset potential versus lithium compared to 0.05 V for conventional graphite anodes has reduced the likelihood of lithium plating. This high energy density and operating voltage, along with a low self-discharge rate and maintenance requirements, have made the Si electrode chemistry more appealing over conventional Li-ion chemistries such as graphite anode systems\textsuperscript{[11]}. Aside from electrochemical characteristics, silicon is a relatively cheap, abundant, and safe material for applications plug-in hybrid electric vehicles (PHEV) and electric vehicle (EV) applications, as well as small-scale consumer electronics.

However, the common issue of Si electrodes is their immense volume changes during charge/discharge cycling. This volume expansion has been shown to be 300 – 400%, which leads to irreversible capacity loss during the initial cycles\textsuperscript{[12]}. This is the primary issue, if not addressed, that restricts Si from practical application. The relation between particle volume expansion and battery failure is evident from a microscopic perspective. When the anode active material is initially exposed to the electrolyte and electrical current is passed through the cell, a solid electrolyte interphase (SEI) layer will be formed on the surfaces of the active material\textsuperscript{[13]}. The formation of the SEI layer is a delicate process, often a coveted trade-secret by battery material manufacturers. If grown to thick, the SEI layer can diminish the electron conductivity, while a fragile SEI layer is likely to fracture and lead to significant losses in active material. Furthermore, the intense volume expansion will induce particle aggregation and, effectively, pressure weld the silicon particles together, reducing the diffusion length of lithium and further increasing the irreversible capacity loss.

In order to preserve and stabilize the original state of the silicon-based anode and
thereby achieve good electrochemical performance, tremendous research efforts have been made in recent years to minimize the mechanical stress induced by the large volumetric changes of silicon. In the following part, recent development of Si-based anode materials is briefly summarized in three categories: Si-C composites, Si-inactive composites and Si-alloy compounds.

1.3.1 Development of Si-C composites

Carbon-silicon core-shell nanowires were developed, in which amorphous silicon was coated onto carbon nanofibers (CNFs) to form a core-shell structure (Figure 1-4a and b) [14]. Since carbon has a much smaller capacity compared to silicon, the carbon core experiences less structural stress or damage during cycling and functions as a mechanical support and an efficient electron conducting pathway (Figure 1-4c and d). The resulted core-shell nanowires have a high capacity of ~2000 mAh/g and improved cycle life compared to Si nanowires (Figure 1-4e). Using these core-shell nanowires, high mass loading and an area capacity of ~4 mAh/cm² were obtained, which are comparable to commercial battery values. However, amorphous silicon was deposited by a CVD approach which is of high cost and difficult to scale up. In addition, the electrodes were fabricated without any binders, which are not compatible with industrial slurry coating approaches.

Figure 1-4. (a, b) Schematic of Si CVD coating onto bare CNFs (a) to make C-Si core-shell NWs (b). (c, d) Transmission electron microscopy (TEM) and selected area...
electron diffraction (SAED) patterns (inset) of a bare CNF (c) and a C-Si core-shell NW (d). (e) Lithiation (red) and delithiation (green) capacity and Coulombic efficiency (CE, blue) versus cycle number for a half cell cycled between 0.1–1 V.[14]

Core-shell design with hollow space in between has been reported to stabilize Li-ion battery electrodes[15]. Commercially available Si nanoparticles are completely sealed inside thin, self-supporting carbon tubes, with rationally designed void space in between the particles and the shells. The well-defined void space allows the Si particles to expand freely without breaking the outer carbon tubes, therefore stabilizing the SEI on the carbon tube surface. High gravimetric capacity (∼1000 mAh/g based on the total mass) and long cycle life (200 cycles with 90% capacity retention) have been realized in this core-shell structured Si electrode. It is worth noting such performance was achieved with very low mass loading (0.1 mg/cm²). Again, no binders were used during fabrication of electrodes. Instead, the freestanding material was directly laminated on copper foil.

It was recently reported a micro-sized pomegranate-like Si-C composite where single silicon nanoparticles are encapsulated by a conductive carbon layer that leaves enough room for expansion and contraction following lithiation and delithiation[16]. Good cyclability (97% capacity retention after 1,000 cycles) and volumetric capacity (1,270 mAh/cm³) were demonstrated. The cycling remains stable even when the areal capacity is increased to the level of commercial lithium-ion batteries (3.7 mAh/cm²). However, the Coulombic efficiency were below 99% during the first 200 cycles, make such a material difficult to be used in a full cell. Moreover, high mass loading electrodes, again, are made in the form of a binder-free microbead/carbon nanotube paper.

A high performance lithium ion anode was developed based on a bottom-up 3-D synthesis approach[17]. First, Si nanoparticles are deposited onto branched carbon-black nanoparticles by a CVD process. Then during an atmospheric pressured CVD deposition of C, the Si-coated carbon-black particles are self-assembled into spherical shaped granules (Figure 1-5a and b). This composite obtained a high
capacity of 1950 mAh/g with a high rate capability (Figure 1-5c). Such high capacity was attributed to the porous network consisting of disordered granules. This composite also has a tap density of 0.49 g/cm³ thanks to its micron particle size. As described above, the preparation involves high-cost CVD process.

In another study, the CVD method was employed to synthesize uniformly deposited continuous Si films on the graphene surface. Then carbon coating was deposited on both sides of the hybrid to alleviate the Si surface oxidation and improve the anode stability. The carbon coated Si/G hybrids exhibited specific capacity in excess of 2000 mAh/g at the current density of 140 mA/g and excellent stability with an average Coulombic efficiency in excess of 99% after 150 cycles. Again, the preparation involves high-cost CVD process. An ultrathick vertically aligned carbon nanotubes (VACNT) electrode coated with Si by decomposition of SiH₄ and a thin C surface layer was designed. The pores remaining within the VACNT electrode are needed for Si expansion during Li insertion. A specific capacity in excess of 3000 mAh/g based on Si alone was achieved. The preparation also used CVD process to

Figure 1-5. (a) Schematic of Si–C nanocomposite granule formation through a hierarchical bottom-up assembly. (b) TEM image showing the highly ordered graphitic structure of the carbon-black surface with a (002) interplanar spacing of 3.34 Å and the amorphous structure of Si. (c) Galvanostatic charge–discharge profiles of the C–Si granule electrode at different charge/discharge rates.¹⁷
deposit Si.

Figure 1-6. Schematic diagram of the synthesis process of conductive-rigid-skeleton-supported Si with TEM images for the intermediate product of Si/B₄C and the final SBG product. (a) Starting materials of micron-sized B₄C and Si. (b) Schematic diagram of the Si/B₄C core–shell structure and TEM image. (c) Schematic diagram of the SBG structure and TEM image.[19]

A core–shell structured Si/B₄C composite with graphite coating was developed by a ball-milling process[19]. Conductive B₄C with high hardness played a dual role in breaking down micron-sized Si and serving as conductive rigid skeleton to support the in situ formed Si particles (Figure 1-6). To further improve the conductivity and stability of the composite the Si/B₄C composite is coated with a few graphitic layers. The Si/B₄C/graphite composite anode shows excellent cyclability with a specific capacity of 822 mAh/g (based on the weight of the entire electrode, including binder and conductive carbon) and 94% capacity retention over 100 cycles at 0.3 C rate. However, the secondary particles are around 100 to 200 nm, giving this composite a low tap density and thus a low volumetric capacity.

Also Si–C core–hollow shell structured 0D/0D nanohybrids were synthesized through a cost-effective and scalable approach[20]. Commercially available Si nanoparticles were oxidized to form a layer of SiO₂ coating. After the as-prepared Si@SiO₂ was coated with a thin layer of amorphous carbon by a gas-phase method, the SiO₂ between the Si core and the surface carbon coating was etched away with hydrofluoric acid, thus creating a void in between Si and C. The resultant core–hollow
shell structured Si–C nanohybrids exhibited significantly improved cycling stability. This improvement was believed to mainly originate from the incorporation of reasonably large voids, which could accommodate the large volume change of Si during cycling as well as the improved electrical conductivity due to the presence of the C shells. Again, the modification of Si nanoparticles with hollow carbon shell did not change much the particle size of the composite, which would lead to a low tap density, typical for nanomaterials.

Graphene-bonded and -encapsulated Si nanoparticles were synthesized by a scalable aerosol method.\textsuperscript{[21]} Si nanoparticles dispersed in an aqueous suspension containing aminopropyltrimethoxysilane (APS) were mixed with a dispersion of GO sheets. The trimethoxysilane group reacts with SiO\textsubscript{2} on the Si nanoparticle surface to functionalize the Si surface. The resultant colloidal mixture was then nebulized to create a mist of aerosol droplets, which were passed through a preheated tube furnace. The amino group on the other end of APS interacts with the carboxylic group on GO to form a strong bond between GO and Si. Upon evaporation of water, the GO sheets first migrated to the surface of the droplets, and then tightly wrapped the Si nanoparticles upon complete evaporation, during which the GO sheets were heavily crumpled due to capillary stress, resulting in the formation of raisin-like graphene-coated Si nanoparticle capsules (Figure 1-7). In such hybrids, the folds and wrinkles of the highly crumpled graphene shells could accommodate the volume expansion of Si upon lithiation without fracture, thus helping to protect Si from excessive SEI deposition while maintaining the electrical contact with Si. As a result, the hybrids showed greatly improved lithium storage performance as LIB electrodes in terms of capacity, cycling stability, and Coulombic efficiency when compared to bare Si nanoparticles. The functionalized Si encapsulated by graphene sample exhibits a capacity of 2250 mAh/g (based on the total mass of graphene and Si) at 0.1C and 1000 mAh/g at 10C, and retains 85% of its initial capacity even after 120 charge/discharge cycles. However, the composite would have low tap density due to its sub-micron secondary particles.
1.3.2 Development of Si-inactive composites and Si-alloy compounds.

Another strategy is to design so called ‘active-inactive’ nanocomposites. The main idea of active-inactive nanocomposite is that the cycling performance of materials reactive to lithium termed as active can be improved significantly when uniformly dispersed in materials that are inert or non-reactive to lithium termed as ‘inactive’ act as the host or matrix. The inactive component plays a very important role as a ‘buffer’ or a ‘matrix’, which endures the large volumetric stresses related to the active species thereby alleviating the mechanical stress arising from volume expansion/contraction during electrochemical cycling. The inactive component can also act as a skeleton for the resulting microstructure, which provides the sites for the reaction at the interface between the active and inactive components.
There are some key points for developing the active-inactive nanocomposites:

1) The active phase should remain interconnected.

2) Matrix systems would need to be identified that exhibit good mechanical strength and ionic/electrical conductivity. In addition, they should be primarily electrochemically inactive against lithium. In other words, the microstructure of the nanocomposite should be able to accommodate any structural change during cycling in order to retain good cyclability.

3) The ratio between active and inactive components also is important in obtaining the desired cyclability because the aggregation of active particles is inversely proportional to the amount of the matrix components used \[^{23}\]. However, with increase in the amount of the inactive component, there is significant reduction in the utilizable capacity.

Silicon oxides (SiO\(_x\), 0<x<2) was investigated as anode through the reduction of SiO\(_x\) in the first discharge process to form, \textit{in situ}, a silicon active phase and the compound Li\(_2\)O as the matrix. Despite the low first cycle (1st cycle) coulombic efficiency and low electronic conductivity, silicon oxides show very promising performance. They typically deliver a capacity of 1000-1700 mAh/g with stable cycling, and could become an effective and low-cost route for preparing silicon-based anodes. In order to have electrodes with the desired specific capacity, an appropriate irreversible capacity and an appropriate amount of inactive phase to buffer volume expansion, the oxygen content in SiO\(_x\) should be optimized to produce materials with a reasonable active/inactive ratio \[^{24, 25}\]. Additional optimization, such as doping \[^{26}\], different binders \[^{27}\], controlled sizes and nanostructure \[^{28}\], carbon coating \[^{29}\] can further improved the performance and make it closer for practical applications.

The other approach is to \textit{ex situ} generate active and inactive phases by typically mechanical milling to form nanocomposite through mechanical alloying. Small grain size along with a ductile inactive phase is significant in order to stabilize the capacity of alloy-type anodes \[^{30}\]. This approach is attractive because of the ease of sample preparation and the lack of chemical reactions between active and matrix components, even upon cycling. In order to generate nanocomposite anodes without inducing any
reaction between the active and inactive components, inactive matrix materials need to be chemically inert against Si. In addition to the chemical inertness, electrochemical inertness is also required to achieve structural integrity, which essentially eliminates oxides. The choice of the inactive matrix materials is limited mainly to non-oxide materials and carbon, which exhibit good electronic and/or ionic conductivity, good mechanical strength, and is light weight. A number of systems have been studied as inactive materials. For example, Kim et al. achieved stable reversible capacities up to 600 mAh/g by embedding silicon particles within nanocrystalline matrices of SiC, TiN, TiB2, and TiC. Dong et al. reported Carbon/Ba–Fe–Si and Fe–Si/C (Figure 1-8) alloy composites showing reversible capacity of ca. 420 mAh/g and 680 mAh/g, respectively. The achieved improvements in the performance by this approach are actually quite limited, probably due to the insufficient structure stability and the continuous growth of SEI during cycling.

![Figure 1-8](image)

**Figure 1-8.** (a) Schematic representation of the deformation process of graphite and Fe–Si alloy particles in mechanical ball-milling and (b) a comparison of the cycling performances of pure Si, Fe–Si alloy and Fe–Si/C composite electrode in the range of 0.02–1.5 V vs. Li+/Li: (■, □) Fe–Si/C composite; (▲, ▼) Fe–Si alloy; (●, ○) pure Si. [36]

### 1.3.3 Development of Si-alloy compounds

Silicon-alloy electrodes, such as NiSi or FeSi, are a type of intermetallic-alloy
electrode with silicon as the active material center and an inactive material, such as Fe or Ni, incorporated into the compound to depart mechanical strength and durability to the electrode during electrochemical cycling. Although Si-alloy electrode materials are emphasized for their ability to accommodate the stresses from active particle expansion, capacity fading still remains the key issue with this battery chemistry. As the intense volume expansion is an inevitable feature with Li-alloy electrodes, related issues such as loss of electrical contact between active material and nanoparticle aggregation are remaining challenges. Furthermore, due to the overwhelming amount of chemical combinations that can compose a Si-alloy, research has been impeded by the slow process of trial-and-error to find the optimal Si-alloy material.

Prior to publications on successful Si-alloy materials and their electrochemical performance, a wealth of literature exists on the failures of Si-alloy inactive phases that, although departing elasticity and mechanical strength to the active material, were insufficient to prevent cycling instability. For instance, Park et al. investigated a Co₂MnSi alloy material for use as an anode in secondary lithium ion cells. Classified as a Heusler alloy, this new class of material was suggested to depart electrochemical stability during charge/discharge, based on other studies, and assist in maintaining the structural integrity of the electrode. Although the evidence of its success was reasonable, the material exhibited an initial charge capacity of ca. 525 mAh/g followed by an immediate decrease to below 200 mAh/g, from which it slowly decreased to ca. 100 mAh/g over 50 cycles (Figure 1-9).
Figure 1-9. (a) Charge–discharge curves of Li/Co$_2$MnSi cell cycled between 0.01 and 3 V at 0.2 mA/cm and (b) cycle performance of Co$_2$MnSi electrode.\textsuperscript{[38]}

Despite the difficult challenges involved with Si-alloy systems, several researchers have announced remarkable achievements and inspired hope for intermetallic-alloy electrodes. Yu et al. synthesized a Si/(FeSiB) powder, where the mechanically-strong less-active FeSiB phase had imparted a high elasticity characteristic to the active material.\textsuperscript{[40]} Furthermore, the successful active material was produced by a potential cost effective and low-temperature process of high-energy ball milling. Galvanostatic charge/discharge testing at 1.0 C-rate over a potential of 0.01 to 1.5 V versus Li/Li$^+$ revealed the impact of ball milling time on the electrochemical performance of the Si-alloy. As shown in Figure 1-10, while the material ball-milled for 6h decreased from ca. 1100 mAh/g to 700 mAh/g over the course of 60 cycles, the material ball-milled for 10h had stable cycling at a capacity ca. 575 mAh/g over the course 100 cycles. Although the specific capacity of the Si-alloy is relatively low, the accomplishment of cycling stability will be a key factor in the application of this material.
Figure 1-10. (a) TEM image and the electron diffraction patterns, (b) SEM image and (c) cycling performance of nanostructured Si/(FeSiB) composite powders obtained by milling for 6 h.\textsuperscript{[40]}

Song et al. reported on a nitrated ternary Si-alloy electrode, composed of silicon, titanium, and nickel (STN).\textsuperscript{[41]} The nickel-titanium alloy (i.e. nitinol matrix) serves as an inactive phase to lithium and imparts an elastic characteristic to the active particle upon lithiation, therefore working to stabilize cycling performance (Figure 1-11a). Similar materials to the STN had been previously investigated\textsuperscript{[42, 43]} with moderate success, however suitable electrochemical performance typically could not be maintained for over 50 cycles. The nitrated STN material reported by Song et al. was synthesized by large-scale adaptable process through the heat treatment of STN.
Figure 1-11. (a) Schematic illustration of pristine STN and nitridated STN electrodes and (b) cycle retentions and coulombic efficiencies at a rate of 1 C of the pristine STN and the nitridated STN electrodes.⁴¹
powders under NH₃ flow. Through this synthesis process, various nitride groups could be formed on the surfaces of the STN powders through the conversion of native metal oxides to nitride compounds. Apparently, the addition of the surface nitride compounds was found to improve mechanical strength, electronic conductivity, specific capacity, and chemical reversibility of the active material. The galvanostatic charge/discharge testing at 0.1 C-rate profile of the nitrated STN material showed a 12 % increase in first charge capacity (916 mAh/g) and 14% increased reversible capacity (849 mAh/g) compared to the bare STN material (Figure 1-11b).


Reference

2013, 9, 2810.


Power Sources **2014**, 253, 282.


Chapter 2: Micro-sized Si-C Composite with Interconnected Nanoscale Building Blocks as High-Performance Anodes for Practical Application in Lithium-ion Batteries

2.1 Introduction

As discussed in Chapter 1, the development of Si-C nanocomposites (e.g., nanowires, nanotubes, or nanoparticles) has been widely studied.[1-10] These nanocomposites proved to be an effective method of improving capacity and cycling stability, since nano-sized Si can alleviate fracture during volume changes and the contact between Si and carbon can maintain electrical contact and improve conductivity of the nanocomposites. However, practical application of nano-sized Si materials in LIBs is difficult. First, achieving a high tap density is important for fabrication of high-energy LIBs for EVs and PHEVs, because it offers a high volumetric energy density. Unfortunately, the tap density of nano-sized materials is generally low, which in turn holds down their volumetric capacity.[11] Furthermore, preparation of nano-sized Si either requires chemical/physical vapor deposition or involves complicated processes, leading to costly, low-yield synthesis that is difficult to scale up to practical levels.[12-14] To date, the abundance of Si has not been fully capitalized upon due to lack of a low-cost strategy for large-scale synthesis of Si anode materials with superior performance.

Micro-sized materials are favorable for practical battery applications since they often enable higher tap density than nano-sized materials and, as a result, are expected to offer higher volumetric capacity.[15, 16] However, the disadvantages of micro-sized Si materials as anodes are obvious. Micro-sized Si particles are more likely to undergo disintegration upon volume change during lithiation/delithiation compared with nano-sized materials, resulting in severe capacity fading.[17] Micro-sized materials also have long ion/electron transport paths that adversely affect high rate
Because of these tradeoffs, it is desirable to develop new materials that combine the advantages of both micro-sized and nano-sized Si materials to improve the cycling performance, rate capability, and energy density of Si anodes.

Such micro-sized Si anode materials with nanoscale building blocks have been previously demonstrated with encouraging results. Cho et al. developed a porous Si-C composite with a nanocrystalline Si framework by a templating approach. The porous Si-C shows excellent electrochemical performance with high capacity and good cycling stability, due to volume change accommodation by its pores. A low cost approach was reported by Cho and Park et al. to produce micro-sized porous Si-C composites by catalytically etching surface layers of micro-sized Si followed by carbon coating. The obtained micro-sized porous Si-C powder shows good cycling stability within the limited number of cycles tested (less than 70 cycles). Yushin et al. reported another type of micro-sized porous C–Si nanocomposite, prepared by physically depositing Si nanoparticles into porous micro-sized carbon granules, exhibited high capacity and good capacity retention. The micro-sized porous C-Si material has a tap density of 0.49 cm$^3$/g and high volumetric capacity of 1270 mAh/cm$^3$ at a current density of 149 mA/g. Micro-sized, carbon-coated Si-based multicomponent anodes composed of Si/SiO cores and crystalline SiO$_2$ shells were developed by Park et. al. and show a high reversible capacity and good capacity retention. However, between these and other reports, there are still few low-cost and scalable approaches for preparing micro-sized Si-C composite anodes with high energy density as well as good cycling and rate performance.

Inspired by the previous findings, we propose that micro-sized Si-C composites should have the following features to obtain excellent electrochemical performance: 1) the size of primary Si building blocks should be small enough to avoid building block fracture induced by volume changes during the lithiation/delithiation process. It has been reported that Si nanoparticles with diameter less than 10 nm can sustain long cycling of lithiation/delithiation without observation of fracture. 2) Si and C should be uniformly mixed at the nanoscale to improve the conductivity but also be highly packed to improve the tap density of the micro-sized particles. 3) The carbon and Si
building blocks should maintain intimate contact even after the micro-sized Si-C particles are pulverized to prevent loss of electrical contact. Following this strategy, we report a new, low-cost, large-scale approach to prepare a micro-sized Si-C composite with excellent performance as an anode material for LIBs. The composite shows a reversible capacity of 1459 mAh/g after 200 cycles at 1 A/g (97.8% capacity retention) and excellent high rate performance of 700 mAh/g at 12.8 A/g, and also has a high tap density of 0.78 g/cm³. The excellent performance of the Si-C composite combined with its low-cost and large-scale synthesis makes it a promising anode material for practical application in LIBs.

2.2 Experimental Section

The synthesis process of the Si-C composite is schematically summarized in Figure 2-1. Commercially available micro-sized SiO is employed as the Si source at a gram scale. The SiO is heated to form a Si/SiO2 composite composed of interconnected Si nanoparticles embedded in an SiO2 matrix due to the disproportionation of SiO. This is followed by removal of the SiO2 via an etching route, transforming the Si/SiO2 composite into porous Si particles. Finally, carbon filling of a large portion of the original pores by thermal decomposition of acetylene creates a micro-sized Si-C composite in which Si and carbon are three-dimensionally interconnected at the nanoscale.

![Figure 2-1](image.png)

**Figure 2-1.** The preparation process from SiO precursor to the Si-C composite.

**Synthesis:** Commercially available SiO powder (325 mesh) from Aldrich was used as the Si precursor. The disproportionation of SiO powder was carried out in a horizontal
quartz tube. In a typical process, high-purity Ar was introduced at a flow rate of 1500 sccm for 20 min to purge the system. Afterwards the flow rate was reduced to 100 sccm and the tube was heated to 950 °C with a ramping rate of 10 °C/min and kept for 5 h. The samples were taken out of the tube at temperatures below 40 °C and immersed in 20 wt% HF solution (H$_2$O: ethanol = 5:1 by volume) at room temperature for 3 h to remove SiO$_2$. The obtained porous Si was collected by filtration and washed with distilled water and absolute ethanol in sequence several times. The final product was dried in a vacuum oven at 60 °C for 4 h. Carbon coating of porous Si was done by thermal decomposition of acetylene gas at 620 °C for 20 min in a quartz furnace. The mixture of acetylene and high-purity argon (argon: acetylene = 9:1 by volume) is introduced at a flow rate of 100 sccm.

Characterization: The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å). The operation voltage and current were kept at 40 kV and 30 mA, respectively. The size and morphology of the as-synthesized products were determined by a JEOL-1200 transmission electron microscope (TEM), FEI Nova NanoSEM 630 scanning electron microscope (SEM) and JEOL-2010F high-resolution transmission electron microscope (HRTEM). The Brunauer–Emmett–Teller (BET) specific surface area of the samples was determined by a Micrometrics ASAP 2020 physisorption analyzer using the standard N$_2$ adsorption and desorption isotherm measurements at 77 K. X-ray photoelectron spectroscopy (XPS) was conducted with a Kratos Analytical Axis Ultra XPS. Raman spectroscopy was conducted with a WITec CMR200 confocal Raman instrument.

Electrochemical measurements: The electrochemical experiments were performed using 2016-type coin cells, which were assembled in an argon-filled dry glovebox (MBraun, Inc.) with the Si and carbon-coated Si electrode as the working electrode and the Li metal as the counter electrode. The working electrodes were prepared by casting the slurry consisting of 60 wt% of active material, 20 wt% of Super P carbon black, and 20 wt% of poly(acrylic acid) (PAA) binder. The mass loading of active materials is about 1.2 mg/cm$^2$ and the thickness of electrodes is about 30 μm. 1 mol/L
LiPF₆ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC: DEC: DMC, 2:1:2 by vol. %) and 10 wt% fluoroethylene carbonate (FEC) was used as the electrolyte (Novolyte Technologies, Independence, OH). The electrochemical performance was evaluated by galvanostatic charge/discharge cycling on an Arbin BT-2000 battery tester at room temperature under different current densities in the voltage range between 1.5 and 0.01 V versus Li⁺/Li. The current density and specific capacity are calculated based on the mass of carbon-coated Si composite.

### 2.3 Results and Discussion

The phases of the precursors and products obtained at different steps in the synthesis process were characterized by X-ray diffraction (XRD). The SiO precursor shows two broad bumps in its XRD pattern (Figure 2-2a), indicating that it is amorphous. After treatment at 950 °C for 5 h, SiO disproportionates to crystalline Si (JCPDS Card No.27-1402 and space group Fd3m [227]) and amorphous SiO₂, as shown in Figure 2-2a. After the removal of SiO₂ by HF etching, a crystalline Si framework was obtained (Figure 2-2a). The broad Si peaks reveal that the as-obtained Si is composed of nanocrystallites with an average size of about 15 nm as estimated by the Debye–Scherrer equation. X-ray photoelectron spectroscopy (XPS) (Figure 2-2b) shows the presence of Si and silicon oxides in the as-obtained material. A strong peak observed at 99.4 eV corresponds to the binding energy of Si(0). A weak bump centered at around 103 eV suggests the presence of silicon oxides that may be caused by the natural oxidation of the Si in air. After carbon deposition, the obtained Si-C composite shows a small bump between 20 and 25 degrees in its XRD pattern (Figure 2-2a), which is attributed to amorphous carbon. Raman spectroscopy (Figure 2-2c) shows two peaks at 1333 and 1614 cm⁻¹ that correspond to the D (disordered) band and the G (graphite) band of carbon, respectively. The ratio of D to G band is estimated to be 2.3, confirming an amorphous carbon structure. The mass
percentage of carbon in the Si-C composite was found to be 20.8% by elemental analysis.

The morphology, size, and structure of the Si-C composite have been investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM studies show that the Si-C composite is composed of micro-sized particles with average diameter of 20 μm (Figure 2-2d) and has similar morphology to SiO precursor powders (Figure 2-3a). This suggests the microscale morphologies are maintained during the disproportionation, etching, and carbon deposition processes. TEM and high-resolution TEM (HRTEM) analyses reveal the structure of the Si-C composite at the nanoscale level. As shown in Figure 2-2e, the Si-C composite contains interconnected Si nanoparticles with a size of about 10 nm. The interconnected feature is clearly exhibited in a high magnification TEM image (Figure 2-3b). An HRTEM image (Figure 2-2f) taken on the edge of an individual composite particle shows many nanocrystallites in which lattice fringes with d-spacing of 3.1 Å are clearly distinguished, corresponding to the (111) crystal planes of the Si. Between these nanocrystallites, amorphous structures are observed and can be ascribed to the carbon. To examine the distribution of carbon in the Si-C composite particles, energy-dispersive X-ray spectroscopy (EDS) mapping was carried out on a cross section of a single Si-C composite particle, as shown in Figure 2-2g. The carbon was found to be uniformly distributed throughout the cross-section of the particle, indicating homogenous carbon filling. The distribution of carbon at nanoscale was also investigated by carbon mapping on a cross section using an energy-filtering TEM (EFTEM). It can be clearly seen in Figure 2-2h and i that carbon is uniformly distributed among Si nanoparticles. The results above demonstrate that micro-sized Si-C composite particles consist of nano-sized Si and C that are three-dimensionally interconnected at the nanoscale throughout the particles.
Figure 2-2. (a) XRD patterns of products obtained at different steps during preparation. (b) XPS spectrum of porous Si. (c) Raman spectrum, (d) SEM image, (e) TEM image, (f) HRTEM image, (g) cross-section SEM and EDS mapping of Si and C in the area marked by the white square, (h) HRTEM and (i) corresponding EF-TEM mapping of carbon in a cross-section of Si-C composite.
It has been well demonstrated that decreasing particle size to the nanoscale and/or introducing carbon can enhance the cycling stability and rate capability of Si-based anode materials.\textsuperscript{[1-10]} Excellent electrochemical performance is thus expected for the Si-C composite. Electrochemical performance of the Si-C composite was characterized by galvanostatic charge/discharge in a coin-cell configuration. The voltage profiles of the Si-C composite and the porous Si without carbon filling at different charge/discharge cycles are shown in Figure 2-4a. The Si-C composite delivers initial discharge and charge capacities of 2004 and 1544 mAh/g at 400 mA/g, respectively, corresponding to a first cycle coulombic efficiency (CE) of 77%. In contrast, the porous Si has discharge and charge capacities of 1970 and 798 mAh/g, respectively, giving a low CE of only 40%. The improved first cycle CE is attributed to the lower specific surface area (87 m$^2$/g vs. 313 m$^2$/g of the porous Si) and stable SEI of the Si-C composite. Lower surface area leads to less side reaction on the Si surface and less irreversible consumption of Li.\textsuperscript{[25-27]} The carbon filling can help to stabilize the formation of the SEI film.\textsuperscript{[28]} The Si-C composite also has a higher
Figure 2-4. (a) Voltage profiles of the porous Si and Si-C composite. (b) Cycling performance of the porous Si and Si-C composite at 400 mA/g. (c) Long cycling performance of the Si-C composite at 1 A/g after first three cycles activated at 400 mA/g. (d) Rate performance of the Si-C composite.

Figure 2-5. CV curve of the Si-C composite electrode measured at a scan rate of 0.1 mV/s for the first cycle.
specific capacity (1675 mAh/g) than the porous Si (1000 mAh/g) at 400 mA/g, as shown in Figure 2-4b. The capacity retention (based on the discharge capacity of the second cycle) of the Si-C composite is 96.6% after 50 cycles. The cyclic voltammetry (CV) curve of the first cycle of the Si-C composite is shown in Figure 2-5. The cathodic peaks below 0.2 V is ascribed to lithiation of Si and the anodic peak around 0.52V is attributed to lithium extraction from Si. A very weak anodic peak around 0.3V due to lithium extraction from SiO$_x$ is also present. This indicates that little amount of SiO$_x$ exists in the Si-C composite, which is consistent with the XPS result (Figure 2-2b). A capacity of 1459 mAh/g after 200 cycles at a higher current density of 1A/g and excellent capacity retention of 97.8% were also attained, with the first three cycles activated at 400 mA/g (Figure 2-4c). The excellent cycling stability is also reflected by the almost overlapped voltage profiles of the 4th and 203rd cycles (Figure 2-4a). The CE increases above 99.5% in 5 cycles and thereafter remains at that level. The Si-C composite also shows excellent high rate capability. As shown in Figure 2-4d, specific capacities of 1100 and 700 mAh/g can be achieved even at high current densities of 6.4 A/g and 12.8 A/g, almost 3 times and 2 times the theoretical capacity of graphite, respectively. The capacity recovers to 1630 mAh/g when the current rate is restored to the initial 400 mA/g, showing the composite’s superior reversibility. The volumetric capacity of the micro-sized Si-C composite is calculated (product of tap density and gravimetric specific capacity) to be 1326 mAh/cm$^3$ at 400 mA/g. The high volumetric capacity is mainly due to the high tap density of the micro-sized Si-C composite (0.78 g/cm$^3$), which is higher than the reported porous C-Si nanocomposite (0.49 g/cm$^3$).

Post-cycling SEM analyses show the morphology change of the Si-C composite electrode after charge/discharge to better understand the reason for such excellent cycling stability and rate performance of the micro-sized Si-C composite. Based on the thickness before (Figure 2-6a) and after lithiation (Figure 2-6b), the volume expansion of the Si-C composite electrode is calculated to be only 44%, similar to the reported result. In addition, a uniform and crack-free film was observed on the top of Si-C composite, indicating a stable SEI layer on the Si-C composite electrode.
Figure 2-6. Cross-sectional SEM images of the Si-C composite electrode before (a) and after (b) lithiation at 400 mA/g. SEM images of SEI layer (c) and lithiated Si-C composite (d) after 10 cycles at 1 A/g. Schematic illustration (e) of the breaking process of the micro-sized Si-C composite during which the interconnected structure and electrical contact is maintained in broken parts.
The SEM investigation on the electrode with the SEI layer removed also clearly demonstrates that the micro-sized Si-C composite particles (Figure 2-7) fragment into smaller particles during cycling, as shown in Figure 2-6d. However, the Si building blocks are still interconnected with carbon in the small particles, maintaining effective electrical contact and good utilization of silicon, as schematically illustrated by Figure 2-6e. To verify this point, a control electrode without using conductive carbon (i.e., Super P) was fabricated and evaluated, which would normally speed up capacity fading because of loss of electrical contact during cycling. The control electrode, however, exhibits similar first cycle CE (74%) and good capacity retention to the electrode with Super P at 1A/g (Figure 2-8a). This result confirms that the micro-sized Si-C composite can maintain electrically-conducting pathways even after fracture and thus achieve excellent cycling stability. It should be noted that the conductive carbon additives are still needed to deliver high rate performance, where the electrical conductivity becomes the dominating limitation (Figure 2-8b).

Figure 2-7. SEM of the Si-C electrode before cycling.
The excellent electrochemical performance of the micro-sized Si-C composite benefits from the nanoscale size of the Si building blocks and the uniform carbon filling. On the one hand, stress in nanoparticles can be easily relaxed without mechanical fracture. The small size also enables short transport pathways for both electrons and Li\(^+\) ions, contributing to high rate capability. On the other hand, the uniform carbon filling offers three advantages. First, the carbon provides an effective physical buffer layer for the volume change of Si upon cycling, which preserves the structural integrity of the silicon building blocks. Second, the carbon filling forms an interpenetrating conductive network connecting the Si building blocks and thus improves the conductivity of the composite. Without carbon in intimate contact with silicon building blocks, electrons have to transport across the whole micro-sized particles to reach the nearest conductive carbon. In our case, the carbon filling forms a conductive network connecting each silicon building block and thus confines the electron transfer path to the nanoscale, which permits rapid charge and discharge. Third, the uniform carbon filling also ensures the maximum utilization of silicon even when the micro-sized particles break into small pieces upon cycling.

2.4 Conclusion

In summary, we have developed a facile route to produce a micro-sized Si-C composite composed of interconnected Si and carbon nanoscale building blocks. The
Si-C composite exhibits a reversible capacity of 1459 mAh/g after 200 cycles at 1 A/g with a capacity retention of 97.8% and has a high tap density of 0.78 g/cm$^3$. Capacities of 1100 and 700 mAh/g can be obtained at high current densities of 6.4 A/g and 12.8 A/g, respectively. The excellent performance is attributed to the nanoscale size of primary particles and interconnected carbon and Si networks which can maintain internal electrical contact and sustain cycling stability. The synthesis method is low-cost and easy to scale up, and is thus believed to have great potential in practical production of high-performance Si materials for Li-ion batteries.
Reference

Chapter 3: Influence of Silicon Nanoscale Building Blocks Size and Carbon Coating on the Performance of Micro-sized Si-C Composite Li-ion Anodes

3.1 Introduction

The development of electric vehicles (EV) and plug-in hybrid electric vehicles (PHEV) requires batteries with high energy density and long cycle lives.\cite{1,2} Li-ion batteries (LIBs) are the dominating candidate for these applications.\cite{3} Current commercial graphite anodes for Li-ion batteries have a theoretical capacity of 372 mAh/g.\cite{4} As increasing anode capacity is one key means of increasing LIBs’ energy density, new anode materials based on abundant, high-capacity silicon (theoretical capacity of 3579 mAh/g) have drawn significant attention as promising alternatives to graphite.\cite{5} However, Si undergoes a large volume change during the lithiation and delithiation processes, causing severe pulverization of Si particles, an unstable solid-electrolyte interphase (SEI) layer, and structural degradation of the electrode— all of which can lead to poor cycling stability.\cite{6,7} Numerous efforts have been made to address these issues, with the main focus on development of Si-based nanomaterials, such as nanowires, nanosprings, nanotubes, and nanoparticles.\cite{8-16} Though Si-based nanomaterials offer high gravimetric capacity and long cycle lifetime, they suffer from intrinsically low tap density, leading to low volumetric capacity,\cite{17} and from expensive preparation which makes large-scale manufacturing difficult.\cite{18-20} Recent work by several researchers has thus focused on materials that combine the advantages of both size regimes, featuring micro-sized particles composed of nanoscale Si building blocks to achieve both high volumetric capacity and stable cycling.\cite{21-24} Especially, SiO provides an ideal platform for preparation of micro-sized anodes with excellent performance such as carbon-coated porous SiO,\cite{25} TiO$_2$-coated SiO,\cite{26} and SiO-C composite.\cite{27} Besides, thermal disproportionation of
SiO proved to be an effective strategy to further improve the performance of micro-sized Si-based anodes.\textsuperscript{[28-30]} For example, Park et al. reported a micro-sized carbon-coated Si-based multicomponent anode composed of Si/SiO cores and crystalline SiO\textsubscript{2} shells that showed a high reversible capacity and good cycling stability.\textsuperscript{[29]} A porous Si-based multicomponent system was developed by Choi and Park et al. through a metal-assisted catalytic etching approach followed by a chemical-assisted thermal disproportionation process. The composite exhibited a stable retention over 100 cycles with a high capacity.\textsuperscript{[30]} We previously demonstrated a micro-sized Si-C composite composed of interconnected Si and carbon nanoscale building blocks \textit{via} a low-cost and scalable route using SiO as starting materials.\textsuperscript{[31]} The Si building blocks are small enough to avoid significant fracture during volume change, while the uniformly distributed carbon ensures high utilization of silicon even when the micro-sized particles crack upon cycling. The composite thus exhibits excellent cycling stability and rate capability, along with a high volumetric capacity due to the high packing of primary particles within the micro-sized particles. However, the 1\textsuperscript{st} cycle coulombic efficiency (CE) is just 77\%, and contribution of Si to the specific capacity of the composite is only around 1930 mAh/g, much lower than the theoretical capacity of Si (3579 mAh/g), so further work to improve the material is still needed.

There are several key parameters that can be tuned in designing such a material. Due to their high volume change, Si building blocks should be kept small enough to prevent serious cracking and thus enable stable cycling. However, smaller building blocks are accompanied by a larger surface area; even a thin layer of natural oxides (SiO\textsubscript{2} and SiO\textsubscript{x} with 0<x<2) would result in a high content of impurities for the whole material, leading to low 1\textsuperscript{st} coulombic efficiency and low specific capacity.\textsuperscript{[32]} Because of this tradeoff, it is necessary to find out the optimized size of Si building blocks to achieve a high capacity without compromising the cycling stability of the composite. Although there are several reports that correlate the effects of particle size to electrochemical performance of Si nanoparticles,\textsuperscript{[33-35]} to the best of our knowledge, no studies are available on the effect of Si building block size within a micro-sized
Si-C composite anode material on its electrochemical performance. Our current synthetic route offers the opportunity to study this effect, since Si building block size can be easily controlled by tuning the thermal disproportionation temperature of SiO, the Si precursor.

Carbon coating also plays an important role in improving the performance of Si-based anodes by increasing electrical conductivity, helping the formation of a better SEI layer, and providing buffer layer for the volume change of Si.\[^{36-38}\] Deposition of carbonaceous gases (C\(_2\)H\(_2\), C\(_3\)H\(_6\), etc) has proved to be an especially effective carbon coating method, particularly for porous Si precursors,\[^{23,39,40}\] for which depositing a thin, conformal coating is usually challenging if other methods are employed. Additionally, carbonaceous gases are reducing agents at high temperature\[^{41}\] and can potentially reduce SiO\(_x\), thereby improving performance. It has been demonstrated by the study of LiFePO\(_4\)/C composites that sp\(^2\)/sp\(^3\) and D/G ratios of carbon prominently affect electrochemical performance.\[^{42}\] However, despite the wide range of temperatures\[^{23,39,40,43}\] and thus resultant structures reported for carbon deposition on Si, the influence of carbon coating temperature on the performance of Si-C composites has not been intensively studied.

Herein, we investigate both the influence of the Si building block size on the performance of micro-sized Si-C composites and the role that carbon coating temperature plays in improving the performance of the composite with the optimized building block size. It has been found that 15 nm is the critical building block size, striking a delicate balance between cycling stability and reversible capacity. On the other hand, carbon coating at higher temperature helps to improve the 1st CE and the rate capability by reducing more SiO\(_x\) (0<x<2) and forming higher-quality carbon. By combining the optimized nanoscale building blocks and carbon coating, we demonstrate that the resultant composite can sustain 600 cycles at 1.2 A/g with a fixed lithiation capacity of 1200 mAh/g.
3.2 Experimental Section

*Synthesis of micro-sized Si-C composites:* The preparation procedures of porous Si are the same as our previous report except for different thermal disproportionation temperature.[31] Three different temperatures of 1100, 1300 and 1400 °C were used and the corresponding products are designated Si-1100, Si-1300 and Si-1400, respectively. Carbon coating of porous Si was done by thermal decomposition of acetylene gas at 620 °C and 800 °C (for Si-1100 only) in a quartz furnace. The mixture of acetylene and high-purity argon (argon: acetylene = 9:1 by volume) is introduced at different flow rates for different duration to make all final Si-C composites have similar carbon content. The resultant products are designated Si-1100-620 and Si-1100-800, respectively.

*Characterization:* The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å). The operation voltage and current were kept at 40 kV and 30 mA, respectively. The size and morphology of the as-synthesized products were determined by a JEOL-1200 transmission electron microscope (TEM), FEI Nova NanoSEM 630 scanning electron microscope (SEM). The Brunauer–Emmett–Teller (BET) specific surface area of the samples was determined by a Micrometrics ASAP 2020 physisorption analyzer using the standard N₂ adsorption and desorption isotherm measurements at 77 K. X-ray photoelectron spectroscopy (XPS) was conducted with a Kratos Analytical Axis Ultra XPS. Raman spectroscopy was conducted with a WITec CMR200 confocal Raman instrument.

*Electrochemical measurements:* The electrochemical experiments were performed using 2016-type coin cells, which were assembled in an argon-filled dry glovebox (MBraun, Inc.) with carbon-coated Si electrode as the working electrode and the Li metal as the counter electrode. The working electrodes, except for those used in rate capability test, were prepared by casting the slurry consisting of 60 wt% of active material, 20 wt% of Super P carbon black, and 20 wt% of poly(acrylic acid) (PAA) binder. The working electrodes for postmortem TEM analysis and rate capability test
were prepared by casting the slurry consisting of 80 wt% of active material and 20 wt% of poly(acrylic acid) (PAA) binder without Super P carbon black. The mass loading on each electrode is about 2 mg/cm². 1 mol/L LiPF₆ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC: DEC: DMC, 2:1:2 by vol. %) and 10 wt% fluoroethylene carbonate (FEC) was used as the electrolyte (Novolyte Technologies, Independence, OH). The electrochemical performance was evaluated by galvanostatic charge/discharge cycling on an Arbin BT-2000 battery tester at room temperature under different current densities in the voltage range between 1.5 and 0.01 V versus Li⁺/Li. The current density and specific capacity are calculated based on the mass of carbon-coated Si composite.

3.3 Results and Discussion

3.3.1 Influence of the Si building block size on the electrochemical performance of Si-C composites

Three porous Si samples were prepared by thermal disproportionation of SiO at three different temperatures (1100 °C, 1300 °C, and 1400 °C) followed by etching with hydrofluoric acid, and were used as precursors for Si-C composites. To exclude the influence of carbon quality and amount, carbon deposition was carried out at the same temperature of 620 °C and the acetylene flow rate was controlled to obtain three Si-C composites with similar carbon contents of around 20 wt% by elemental analysis. The materials disproportionated at 1100 °C, 1300 °C, and 1400 °C were designated Si-1100-620, Si-1300-620, and Si-1400-620, respectively. For comparison, the material disproportionated at 950 °C [31] (named Si-950-620) is included in the following discussion. The phase and crystallinity of the three materials were examined by X-ray diffraction (XRD). As shown in Figure 3-1a, the peaks of all patterns can be indexed to those of crystalline face-centered cubic Si (JCPDS Card No.27-1402). The peaks become narrower as temperature increases, indicating increased crystalline domain size. The morphology, structure, and size of the Si-C composites were investigated by scanning electron microscopy (SEM) and
transmission electron microscopy (TEM). All samples are composed of micro-sized particles with a size of up to 30 μm (Figure 3-1b), similar to the SiO precursor (Figure 3-2), suggesting the microsize nature has been well inherited. However, while Si-1100-620 and Si-1300-620 were irregularly-shaped particles, the Si-1400-620 particles were instead rounded (Figure 3-3), which may be due to further growth of particles at higher temperature. The difference in building block size is revealed by TEM. All samples are composed of interconnected Si nanoparticles, however, the particle size increases from 10 nm for Si-950 to 15 nm for Si-1100, to 30 nm for Si-1300, and further to 80 nm for Si-1400, as shown in Figure 3-1c-f and Figure 3-3b-d. Correspondingly, the carbon layer on each building block becomes thicker as the particle size increases and surface area commensurately decreases.
Figure 3-1. (a) XRD patterns of Si-950-620, Si-1100-620, Si-1300-620 and Si-1400-620. (b) Typical SEM image of Si-1100-620 and Si-1300-620, and TEM images of (c) Si-950-620, (d) Si-1100-620, (e) Si-1300-620 and (f) Si-1400-620. XRD pattern and TEM image of Si-950-620 are reproduced from Chapter 2 for comparison.

Figure 3-2. SEM of SiO precursors.
Galvanostatic charging/discharging was employed to evaluate the electrochemical performance of all Si-C composites as Li-ion anode materials. The initial voltage profiles at a current density of 400 mA/g are shown in Figure 3-4a. The initial discharge and charge capacities of Si-1100-620 are 2519 and 1962 mAh/g, respectively, giving a first cycle CE of 78%. Si-1300-620 delivers initial discharge and charge capacities of 2752 and 2253 mAh/g, respectively, corresponding to a first CE of 82%. Si-1400-620 exhibits a higher CE of 84%, with discharge and charge capacities of 3312 and 2778 mAh/g, respectively. Although it has a lower initial
capacity and initial CE, Si-1100-620 shows stable cyclability at 1 A/g with the 1st cycle activated at 400 mA/g (Figure 3-4b). A capacity of 1800 mA/g was obtained after 100 cycles with no noticeable capacity fading compared to the discharge capacity of the second cycle. In contrast, the capacity of Si-1300-620 was only stable for 20 cycles and then started to fade quickly. Si-1400-620 showed the worst cycling stability, as the capacity fading happened at the very beginning.

![Figure 3-4. First cycle voltage profiles and cycling performance of Si-950-620, Si-1100-620, Si-1300-620 and Si-1400-620. Specific capacities are calculated based on the weight of Si-C composites. Voltage profile and cycling performance of Si-950-620 are reproduced from Chapter 2 for comparison.](image)

Given the carbon content of around 20 wt% and neglecting the capacity of carbon, the specific capacity based only on the mass of Si in the composites is 2452, 2816, and 3472 mAh/g for Si-1100-620, Si-1300-620, and Si-1400-620, respectively. While the capacity of Si in Si-1400-620 is close to the theoretical value, the capacity of Si in Si-1100-620 is far from that. As found in our previous study, silicon oxides (SiO₂ and SiOₓ with 0<x<2) exist in porous Si due to natural oxidization.[31] These oxides lead to lower reversible capacity and 1st cycle CE not only because of the dead weight of inactive SiO₂, but also because of the irreversible formation of Li₂O and Li₄SiO₄ during the initial lithiation of SiOₓ.[32] In addition, Li₂O and Li₄SiO₄ could act as a constraining shell that limits the expansion and thus the extent of lithiation of Si core by introducing compressive stress, further decreasing reversible capacity.[44] However, despite lower capacity, the presence of surface oxides may improve the cycling
stability as demonstrated in a previous report.\cite{45} A larger surface area should result in a higher content of silicon oxides. The specific surface area, reversible capacity, 1st cycle CE and cyclability of the three samples are summarized in Table 3-1. Among the three porous samples, Si-1100-620 has the highest surface area due to its smallest particle size. It is clear that the reversible capacity and the 1st CE are directly related to the Si building block size and inversely related to the surface area, whereas the cycling becomes more stable as the building block size decreases. The result of our previous study,\cite{31} in which the Si-C composite (Si-950-620) with 10 nm Si building blocks showed a reversible capacity of 1930 mAh/g (based on the mass of Si in the composite) and a 1st CE of 77%, is consistent with this trend.

Table 3-1. Summary of building block size, surface area, reversible capacity, 1st cycle CE and cyclability of various Si-C composites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Size of Si building blocks (nm)</th>
<th>Surface area* (m²/g)</th>
<th>Reversible capacity of Si-C composite and Si alone (mAh/g)</th>
<th>1st cycle CE</th>
<th>Cyclability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-950-620\cite{31}</td>
<td>10</td>
<td>313</td>
<td>1544/1930</td>
<td>77%</td>
<td>Excellent</td>
</tr>
<tr>
<td>Si-1100-620</td>
<td>15</td>
<td>286</td>
<td>1962/2452</td>
<td>78%</td>
<td>Excellent</td>
</tr>
<tr>
<td>Si-1300-620</td>
<td>30</td>
<td>92</td>
<td>2253/2816</td>
<td>82%</td>
<td>Stable for 20 cycles</td>
</tr>
<tr>
<td>Si-1400-620</td>
<td>80</td>
<td>58</td>
<td>2778/3472</td>
<td>84%</td>
<td>Fading from the beginning</td>
</tr>
</tbody>
</table>

* N₂ sorption isotherms and pore size distribution are presented in Figure 3-5.
Figure 3-5. (a, c and e) N\textsubscript{2} sorption isotherms and (b, d and f) pore size distribution of Si-1100-620, Si-1300-620 and Si-1400-620.

To better understand the different cyclabilities of the Si-C composites with different building block sizes, SEM and TEM analyses were carried out on delithiated Si-C composite electrodes after 100 cycles. In the case of Si-1100-620, despite the cracks shown in Figure 3-6a, contours of single particles can clearly be seen in the high magnification image in Figure 3-6b, indicating that growth of the SEI layer has been efficiently limited. In comparison, parts of the Si-1300-620 electrode (Figure 3-6c) and nearly all of the Si-1400-620 electrode (Figure 3-6d) are buried under a
thick SEI layer, which suggests unstable SEI growth during cycling. It should be noted that severe charging as a result of the insulating nature of SEI layer prevented us from obtaining clear high-magnification images for Si-1300-620 and Si-1400-620 electrodes. Additionally, much of the active material on the Si-1400-620 electrode was found to have peeled away from the current collector after cycling. The differences mentioned above serve as strong evidence that Si-C composites with smaller building blocks can much more effectively mitigate the unstable growth of the SEI layer upon cycling. Insight at the nanoscale level was gained by TEM. Because Super P is similar in size (Figure 3-7) to the building blocks of Si-1300-620 and Si-1400-620 and would not degrade upon cycling, electrodes for postmortem TEM observation were prepared without Super P (Si-C composite and binder in an 8:2 ratio). The electrolyte, SEI layer, and binder were removed by washing with acetonitrile and 1M hydrochloric acid solution. The morphology and interconnectedness of the building blocks are similar to those of the pristine composites, except that the size of Si slightly increased (Figure 3-6e-g), consistent with the previous in-situ study of Si nanoparticles.[46] However, as mentioned previously, when opening the cells we found that a large part of the active material on the Si-1400-620 electrode was peeling off of the current collector, while the Si-1100-620 and Si-1300-620 electrodes appeared largely intact.
Figure 3-6. SEM images of electrodes with different Si-C composites after 100 cycles: (a) low and (b) high magnification images of Si-1100-620, (c) Si-1300-620, and (d) Si-1400-620. TEM images of different Si-C composites after 100 cycles: (e) Si-1100-620, (f) Si-1300-620, and (g) Si-1400-620.
Based on the cycling performance and the SEM and TEM analyses after cycling, we propose that the core mechanisms by which volume change of micro-sized Si-C composites affects cyclability is by influencing SEI growth and electrode structural integrity, as schematically shown in Figure 3-8. Large volume change can break the SEI layer and expose fresh material to the electrolyte, leading to continual SEI growth. As the SEI layer grows, it will increase cell impedance by both raising the barrier to Li$^+$ ion diffusion and electrically insulating particles of the composite from one another, and may eventually consume enough electrolyte to kill the cell.[6] The larger SEI layers on larger Si-C building blocks are particularly vulnerable to breaking during volume change of the underlying silicon, as larger nanoparticles have been
shown to release more energy when cracking and thus be more prone to it.[47] A robust SEI layer is formed on the surface of Si-1100-620 during the initial cycle and remains stable in later cycles due to the small size of the Si building blocks. The SEI stability is evidenced by the average CE of 99.76% from the 2\textsuperscript{nd} to 100\textsuperscript{th} cycles (Figure 3-9), among the best for published Si anodes.[11] Although the Si building blocks of Si-1300-620 do not themselves break, their SEI layer cracks as the Si expands and contracts, inducing the formation of new SEI by exposing fresh Si surface to electrolyte. The continuous formation of SEI is verified by the low coulombic efficiency of around 98% even while the capacity was stable (Figure 3-9). As the SEI grows thicker, the electrical contact between particles and lithium diffusion to particles decrease and likely hit a critical value, leading to capacity fading after 20 cycles. With the largest building blocks, Si-1400-620 has the worst situation. The SEI layer becomes even more unstable, with CE of about 97% (Figure 3-9), and the electrode also undergoes fast structural degradation – evidenced by its severe peel-off after cycling – resulting in capacity fading at the very beginning due to the loss of electrical contact.
Figure 3-8. Scheme of evolution of SEI layer on Si building blocks and electrode structure of different micro-sized Si-C composites upon cycling.
3.3.2 Influence of carbon coating on the electrochemical performance of the Si-C composite

To determine the influence of carbon coating on the performance of Si-C composites, carbon-coating was also performed at a higher temperature. The Si material prepared at 1100 °C was chosen for this study due to its stable cyclability. The acetylene deposition was carried out at 800 °C with a controlled flow rate to obtain a new composite, namely Si-1100-800, with the similar carbon content (about 20 wt% by elemental analysis) to Si-1100-620 so that the effects of carbon content can be excluded.

No discernible differences were found between XRD patterns or TEM images of Si-1100-800 (Figure 3-9 and Figure 3-11) and Si-1100-620 (Figures 3-1a and 3b). Figure 3-12a shows the Raman spectra of Si-1100-620 and Si-1100-800 in the...
wavenumber range containing carbon bands. Peaks around 1600 cm$^{-1}$ and 1340 cm$^{-1}$ are present for both composites and correspond to the G (graphitic) and D (disordered) bands of carbon, indicating that the carbon coatings are composed of amorphous carbon.$^{[29]}$ However, the D/G ratio of Si-1100-800 is estimated to be 2.1, lower than the 2.3 of Si-1100-620, which suggests a higher degree of graphization and a lower content of sp$^3$ carbon at higher deposition temperature.$^{[48]}$

**Figure 3-10.** XRD pattern of Si-1100-800.
The influence of carbon deposition temperature on the underlying Si was investigated by performing X-ray photoelectron spectroscopy (XPS) on porous Si, Si-1100-620, and Si-1100-800, as shown in Figure 3-12b. The peaks around 99.5 eV and 103.4 eV are assigned to Si(0) and Si(4+), respectively, and the binding energies in between correspond to SiO\textsubscript{x} (0<x<2).\textsuperscript{[11,49]} The shift of Si(0) binding energy probably results from different oxidation state of materials.\textsuperscript{[50]} It is clear that Si is partially oxidized after carbon coating even under Ar atmosphere (Grade 5.0 Ar is used), consistent with previous findings.\textsuperscript{[51]} The key difference between Si-1100-620 and Si-1100-800 is that, as carbon coating temperature increases, the intensity of the SiO\textsubscript{x} region decreases and the intensity of the Si(4+) peak (corresponding to SiO\textsubscript{2}) increases relative to the intensity of the Si(0) peak, which may be due to disproportionation of SiO\textsubscript{x} and/or its reduction by acetylene.\textsuperscript{[49]} To determine whether overall oxide content increases or decreases (whether increase of SiO\textsubscript{2} or decrease of SiO\textsubscript{x} is dominant), Raman spectra were collected for the three materials (Figure 3-12c). A strong peak at 510 cm\textsuperscript{-1} and two broad peaks around 300 and 935 cm\textsuperscript{-1} are observed for porous Si, corresponding to characteristic peaks of nanoscale Si.\textsuperscript{[52]} Porous Si also shows a weak broad bump around 350 cm\textsuperscript{-1}, which is assigned to amorphous SiO\textsubscript{2} and SiO\textsubscript{x} (0<x<2).\textsuperscript{[53]} After carbon deposition at 620 °C, the peak corresponding to SiO\textsubscript{2} and SiO\textsubscript{x} (0<x<2) becomes more prominent while the two
broad peaks around 300 and 935 cm\(^{-1}\) become much weaker, which agrees well with the XPS results. However, with a carbon deposition temperature of 800 °C, the peak related to SiO\(_2\) and SiO\(_x\) (0<x<2) can hardly be observed, indicating that the overall silicon oxide content decreases (decrease of SiO\(_x\) prevails over the increase of SiO\(_2\)). We propose that this difference results from the difference in competition between oxidation (by oxygen residue after purging with Ar and the miniscule amount of oxygen in the Ar itself) and reduction (by acetylene on the surface of Si) at different temperatures.\([41,54]\) The porous Si tends to be partially oxidized by oxygen due to the relatively weak reducing ability of the acetylene when the temperature is low. At higher temperature, acetylene can partially reduce SiO\(_x\) to Si. The variance in reducing ability may be due to different decomposition mechanisms of acetylene at different temperatures, as described in previous work.\([55]\)

**Figure 3-12.** (a) Raman spectra of Si-1100-620 and Si-1100-800 around carbon region; (b) XPS spectra of Si-1100, Si-1100-620 and Si-1100-800; (c) Raman spectra of Si-1100, Si-1100-620 and Si-1100-800 around silicon region.
The electrochemical performance of Si-1100-800 is shown in Figure 3-13. Si-1100-800 exhibits a 1st cycle CE of 86% (Figure 3-13a), which is much improved from the 78% 1st cycle CE of Si-1100-620, along with excellent capacity retention (Figure 3-13b) and initial discharge and charge capacities of 2250 and 1942 mAh/g, respectively. The rate performance of Si-1100-620 and Si-1100-800 were also studied. To examine the effect of carbon coating only, electrodes for the rate capability test were prepared without Super P carbon additive (Si-C composite and binder in an 8:2 ratio). As shown in Figure 3-13c, both of the electrodes have similar capacity retention at relatively low current densities. However, a noticeable difference was found at high rate. A capacity of 990 mAh/g was achieved at 6.4 A/g by Si-1100-800, corresponding to retention of 49% based on the capacity at 400 mA/g. In contrast, at the same current density, Si-1100-620 only delivered 610 mAh/g (a retention of 31%). This difference was further studied by electrochemical impedance spectroscopy (EIS) measurements (Figure 3-13d) on Si-1100-800 and Si-1100-620 cells after the rate capability test. The semicircle on the EIS spectrum of Si-1100-800 is smaller than that on the spectrum of Si-1100-620, indicating that Si-1100-800 has a lower charge transfer resistance.[56]
Figure 3-13. (a) First cycle voltage profile and (b) cycling performance of Si-1100-800 electrode. (c) Rate performance and (d) Impedance spectra measured after rate capability test of Si-1100-620 and Si-1100-800 electrodes without Super P.

The improvement in both the 1st cycle CE and rate capability of Si-1100-800 can be attributed to the synergistic effect of better carbon quality and reduction of SiOₓ at higher deposition temperature. Si-1100-800 has a more graphitic carbon coating, which helps to form a more compact SEI layer and thus achieve a higher CE. In addition, with less SiOₓ, the irreversible consumption of Li⁺ by formation of Li₂O and Li₄SiO₄ should be lessened, giving a higher 1st CE. The enhanced rate performance of Si-1100-800 is attributed to the composite’s higher electrical conductivity, which also comes from both reduction of SiOₓ and improved carbon quality. Firstly, formation of less Li₂O and Li₄SiO₄ leads to lower resistance, as they are electrically insulating; secondly, carbon formed at 800 °C has lower D/G ratio and higher sp³ content and as a result has higher electronic conductivity, agreeing well with the study on LiFePO₄/C composites that sp²/sp³ and D/G ratios closely correlate with electrochemical performance. Previous investigation on carbon coating of multi-dimensional bulk Si anodes at different temperatures of 700, 900 and 1000 °C shows that carbon deposited at 900 °C has the highest degree of graphitization (D/G ratio of 2.1) and the resultant composite exhibits the best electrochemical performance. Based on the current and previous findings, the upper limit of carbonization temperature should be in the range of 800 to 900 °C.
Figure 3-14. (a) The cycling performance and (b) voltage profiles of Si-1100-800 electrode with a constant discharge (lithiation) capacity of 1200 mAh/g between 1.5 to 0.01V at 1.2 A/g after first six cycles activated at 600 mA/g.

To demonstrate the long-term cyclability of the Si-C composites, the optimized Si-1100-800 was cycled with the fixed lithiation capacity of 1200 mAh/g at a rate of 1.2 A/g between 0.01 to 1.5V. These conditions were chosen because: 1) it has been demonstrated that the cycle life of Si-based anodes can be extended by controlling the amount of lithium that alloys with the silicon,[61,62] and 2) replacing the presently-used carbonaceous anodes with anodes having capacity on the order of 1000 to 1200 mAh/g would grant a significant improvement in the specific capacity of Li-ion batteries.[63,64] As shown in Figure 3-14a, the charge capacity was maintained well for 600 cycles. The first cycle CE is 81% and the average CE from the 2\textsuperscript{nd} to the 600\textsuperscript{th} cycle is 99.51%. Figure 3-15b plots the corresponding discharge–charge voltage profiles at different cycles, which remain similar in shape aside from the lithiation voltage slowly decreasing. As far as we know, this is the best cycling performance with such a high capacity for micro-sized Si-based anodes.[65]

3.4 Conclusion

In summary, the Si building block size of micro-sized Si-C composites has been effectively controlled by varying the disproportionation temperature of the SiO precursor, and its influence on electrochemical performance of the composites has
been investigated. The 1st cycle coulombic efficiency and reversible capacity of the Si-C composites increase as building block size increases, while cycling stability plummets. 15 nm was found to be the critical size that enables both high reversible capacity and excellent cycling stability. The 1st cycle CE and high rate performance can be greatly improved by carbon coating at a higher temperature of 800 °C, because more SiO_x (0<x<2) is reduced and carbon of better quality is formed. Stable cycling for 600 cycles at a rate of 1.2 A/g with a fixed lithiation capacity of 1200 mAh/g was achieved by the micro-sized Si-C composite prepared with the optimized nanoscale building block size and carbon coating temperature. We expect that the present findings will aid future design and preparation of high-performance micro-sized Si-C composites.
Reference


Chapter 4: Improved Rate Capability of Si-C Composite Anodes
by Boron Doping for Lithium-ion Batteries

4.1 Introduction

The fast-growing demands of portable electronics and electric vehicles require lithium-ion batteries (LIBs) with high energy and power densities [1]. The low specific capacity (372 mAh/g) of graphite, a common anode material in commercial LIBs, are major barriers to meeting these demands [2]. Silicon has been investigated as one of the most promising alternatives to graphite due to its high specific capacity (>3500 mAh/g) and abundance [3]. However, silicon suffers from low power output, mainly because its electronic conductivity is low [4].

Great efforts have been devoted to enhancing the rate capability of Si-based anodes, with major attentions paid to geometry tailoring, such as decreasing dimensions of Si particles to the nanoscale level to shorten transport pathways for both electrons and Li$^+$ ions [5,6], and composition modification, such as preparing various Si-C and Si-conductive polymer composites to improve surface electronic conductivity [7,8]. Even though exciting results have been achieved by such strategies, the electronic conductivity of Si itself remains low due to its intrinsic semiconductor nature, which limits the further improvement of rate capability. Carrier doping has been well established as an effective way to increase electronic conductivity of Si in the semiconductor industry [9]. However, in the field of LIBs, doping silicon with elements such as boron has been mainly employed to produce porous Si materials by wet etching [10], while the effects of doping on the rate capability of Si-based anode materials have not been intensively studied. Wang et al. reported phosphorus-doped Si film on virus enabled 3D current collectors using a physical vapor deposition technique, which exhibited improved rate performance [11]. We previously demonstrated a micro-sized Si-C composite featuring interconnected Si and carbon nanoscale building blocks that showed excellent cycling stability and rate capability.
The synthetic route can be easily extended to prepare doped Si-based composites by simply introducing dopant precursors during thermal disproportionation of SiO. Herein, we report a facile preparation of a boron-doped Si-C composite (B-doped Si-C) and investigate the effects of boron doping on rate capability.

4.2 Experimental Section

The preparation procedures of boron-doped micro-sized Si-C composite are the same for our previously reported Si-C composite [12], except a mixture of SiO powder (325 mesh, Sigma Aldrich) and B₂O₃ powder (Alfa Aesar) with molar ratio of Si: B as 10:1 was used as the starting material. The products before and after carbon coating are designated B-doped Si and B-doped Si-C, respectively. Undoped micro-sized Si-C composite is also produced for comparison and designated Si-C.

The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu Kα radiation. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images were taken by a FEI Nova NanoSEM 630 and JEOL-1200. X-ray photoelectron spectroscopy (XPS) was conducted with a Kratos Analytical Axis Ultra XPS. Raman spectroscopy was performed with a WITec CMR200 confocal Raman instrument.

Electrochemical experiments were performed using coin cells with Li metal as the counter electrode. The working electrodes consists of 80 wt% of active material and 20 wt% of poly(acrylic acid) binder. 1 M LiPF₆ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (2:1:2 by volume) and 10 wt% fluoroethylene carbonate was used as electrolyte. The mass loading of active materials is 1.2 mg/cm². Galvanostatic charge/discharge tests were carried out on an Arbin BT-2000 battery tester between 1.5 and 0.01 V versus Li⁺/Li. Electrochemical impedance spectroscopy (EIS) was carried out by applying a perturbation voltage of 5 mV between 10 mHz and 100 KHz using a Solartron SI 1260 impedance analyzer. Powder conductivity was measured using a Solartron SI 1287 electrochemical interface.
4.3 Results and Discussion

The phase and crystallinity of Si-C and B-doped Si-C were examined by XRD. Peaks of both XRD patterns can be indexed to those of face-centered cubic crystalline Si (JCPDS Card No.27-1402), as shown in Figure 4-1. Compared to undoped Si-C, the peaks of B-doped Si-C shift to higher angles due to the replacement of Si atoms by smaller B atoms which leads to a smaller lattice constant [13]. This result, combined with the absence of Si-B alloy peaks, indicates the successful doping of B into Si. No discernable difference in peak intensities can be found, suggesting that B doping did not affect crystallinity of the final product.

![XRD patterns of Si-C and B-doped Si-C.](image)

**Figure 4-1.** XRD patterns of Si-C and B-doped Si-C.
The nature of Si and B in B-doped Si before carbon coating was investigated by XPS. As shown in the Si 2p spectrum in Figure 4-2a, the strong peak at 99.4 eV corresponds to the binding energy of Si(0) [14]. A broad weak bump is also observed around 103 eV, which suggests the existence of silicon oxides [15]. Figure 4-2b shows the B 1s spectrum, which is rough due to the very low relative sensitivity of boron [16]. The peak centered at 188 eV is attributed to B(0) [16], serving as direct evidence of B doping. The content of B is calculated to be 4.1% (atomic percentage) by XPS survey, close to the designated composition of 5%. Raman spectroscopy was employed to further study the B-doped Si after carbon coating. The Si peak shifts from 510 cm\(^{-1}\) for undoped Si to 494 cm\(^{-1}\) for B-doped Si (Figure 4-2c) due to disorder in the Si structure caused by the stress developed in the surrounding Si atomic network after B doping, which is consistent with the previous report [17] as well as with XRD and XPS results above. It has been reported that B doping into carbon can enhance electrochemical performance of resultant B-doped carbon [18,19]. However, in our case B in carbon was not detected as shifting of C peaks is not observed [18]. As shown in Figure 4-2c, both spectra show peaks around 1330 and 1610 cm\(^{-1}\), corresponding to the D and G band of carbon, respectively [12]. The absence of B in carbon is due to the moderate carbon coating temperature of 620 °C, much lower than the temperature (900-2800 °C) required for B doping in carbon via solid state diffusion [19,20].

The morphology, size, and structure of the B-doped Si-C composite were also investigated by SEM and TEM. The SEM image in Figure 4-2d shows that the B-doped Si-C is composed of micro-sized particles with an average size of about 20 μm. TEM study reveals that these micro-sized particles are built up of interconnected nanoparticles with a size of about 10 nm (Figure 4-2e and 2f). This shows that B doping has no influence on the size and structure of product, as the same features are observed for the undoped Si-C composite [12].
The doping effects on the electrochemical performance was evaluated by galvanostatic charge/discharge at different current densities. To examine the effects of B doping only, potential interference factors were excluded. First, electrodes were prepared without any external carbon additive. Second, to exclude the influence of carbon content, a similar carbon content of around 20 wt% (measured by elemental
analysis) was achieved for both B-doped Si-C and Si-C.

Figure 4-3. (a) Rate performance and (b) capacity ratio at different current densities of B-doped Si-C and Si-C. (c) Voltage profiles at different current densities of B-doped Si-C. (d) Impedance spectra of B-doped Si-C and Si-C.

As shown in Figure 4-3a, B-doped Si-C exhibits similar specific capacity to Si-C at 400 mA/g due to the low content of B as discussed above. However, the difference in capacity can easily be observed at higher current densities. For example, Si-C can only achieve 323 mAh/g cycling at 6.4 A/g. In comparison, a capacity of 575 mAh/g (volumetric capacity of 449 mAh/cm³ based on tap density of 0.78 g/cm³) can be obtained for B-doped Si-C, about 80% higher than that of Si-C and 1.5 times the theoretical capacity of graphite. Note that this capacity was achieved without addition of any external conductive additive, which is usually present in large quantity (more than 20 wt%) in reports on Si-based materials with good high rate performance [10]. After the current density was restored to 400 mA/g, B-doped Si-C showed better stability than Si-C with similar capacity. The coulombic efficiency (CE) of B-doped
Si-C remains above 99.5% at various rates. To further investigate the cycling stability at high rates, the current density was increased from 400 mA/g to 6.4 A/g again. In contrast to the obvious capacity fading of Si-C, the capacity of B-doped Si-C was stable for about 50 cycles at 6.4 A/g. Figure 4-3b plots the ratio of specific capacities of B-doped Si-C and Si-C at different current densities. It is clear that the difference in specific capacities becomes more and more striking with increasing current density. The voltage profiles of B-doped Si-C at various current densities are shown in Figure 4-3c. The first cycle CE is 73.7%, similar to that of Si-C (Figure 4-3a). The kinetic feature of charge/discharge curves is maintained at high rates, as the voltage profiles remain similar in shape with increasing current density, indicating a facile charge transport process. To understand the reason for the better rate capability of B-doped Si-C, cells were analyzed by the EIS measurements after rate capability testing at delithiated state (Figure 4-3d). The inclined line in the low frequency region is related to Li-ion diffusion within particles [21]. The difference is indicative of change in Li-ion diffusion behaviors due to boron doping, which agrees well with the report that addition of dopants such as boron and phosphorus to Si strongly influences the energetics and kinetics of Li insertion [22]. B-doped Si-C shows a smaller semicircle in high-to-medium frequency region than Si-C, which suggests a lower charge transfer resistance [21]. The electronic conductivities of B-doped Si-C and Si-C powder were also measured according to a reported protocol [23]. Compared to 9.6x10^{-6} S/m of Si-C, B-doped Si-C has higher conductivity of 3.6x10^{-4} S/m. The results indicate that boron doping leads to an increase in electronic conductivity of the Si-C composite and thus improves its rate capability.

4.4 Conclusion

In summary, a boron-doped Si-C composite has been successfully prepared and the boron doping was confirmed by XRD, XPS, and Raman spectrometry. The effects of boron doping on the rate capability of the Si-C composite have been investigated. Compared to undoped Si-C, the B-doped Si-C composite exhibits much improved rate
capability. A high capacity of 575 mAh/g can be achieved by B-doped Si-C at 6.4 A/g, about 80% higher than that of Si-C. The improved rate capability is attributed to lower charge transfer resistance of B-doped Si-C, as shown by EIS measurement. The finding demonstrates that boron doping is an effective approach to enhance rate capability of Si-based anodes for LIBs.
Reference


Chapter 5: Dual Conductive Network-Enabled Graphene/Si-C Composite Anode with High Areal Capacity for Lithium-ion Batteries

5.1 Introduction

Lithium-ion batteries (LIBs) have been intensively studied because of their relatively high energy density, which makes them attractive for use in many electronic devices [1]. Recently, the emerging market for electric vehicles requires LIBs with higher energy density [2, 3]. Developing new anode materials with high specific capacity is an effective way to increase the energy density of LIBs. Due to its high theoretical capacity (3579 mAh/g) and abundance, silicon has been regarded as one of the most promising alternatives to the currently-used graphite anode, which has a low theoretical capacity of 372 mAh/g [4, 5]. However, there is a major barrier to the practical application Si: its large volume change during charge/discharge causes to severe pulverization of Si particles and degradation of Si electrodes, leading to poor cycling stability [6]. Extensive efforts have been devoted to improving the cyclability of Si-based anodes with encouraging results, including development of various Si nanostructures/nanocomposites, novel binders and electrolyte additives [7-16].

However, most of the advances in Si-based materials to date were reported in the form of gravimetric capacity (mAh/g), while areal capacity (mAh/cm²) has rarely been discussed. Gravimetric capacity describes the capacity that a material can deliver. However, in practical applications the performance of anodes is evaluated at the electrode level, and areal capacity is an indication of the energy that an electrode can store. Although high gravimetric capacity of Si-based materials can be achieved, it usually comes with very low mass loading, which in turn leads to electrodes with limited areal capacity [11, 13]. In the few reports involving high mass loading, higher areal capacity was demonstrated with: 1) limited cycle numbers; 2) fixed gravimetric
We previously demonstrated a micro-sized Si-C composite composed of interconnected Si nanoscale building blocks and carbon conductive network [22-24]. However, the conductive network is only within the micro-sized particles and no such a network exists between particles, potentially leading to large interparticle contact resistance. Due to its extraordinary electronic conductivity and two-dimensional morphology [25, 26], graphene has been identified as an excellent conductive additive in various composites to enhance the electrochemical performance of electrode materials by improving electron transport and maintaining electrical contact in electrodes [27-31]. However, graphene has majorly been incorporated with nanomaterials to form nanocomposites and graphene-containing micro-sized composites have been less reported.

Herein, we report a novel micro-sized graphene/Si-C composite (G/Si-C), in which micro-sized Si-C particles are wrapped by graphene sheets. The two-dimensional conductive graphene sheets act as a conductive network between particles and thus decrease the contact resistance of the whole electrode. Thanks to it having conductive networks both within single particles and between different particles, G/Si-C shows a higher degree of material utilization at high mass loading compared to the raw micro-sized Si-C composite (Si-C). An areal capacity of 3.2 mAh/cm² after 100 cycles and high coulombic efficiency (average 99.51% from 2nd to 100th cycle) are achieved by G/Si-C, comparable to that of commercial LIBs [32], making it a promising anode material for practical applications in LIBs.

5.2 Experimental Section

Synthesis of G/Si-C: Graphite oxide (GO) was firstly prepared from natural graphite powder (300 mesh, Alfa Aesar) by a modified Hummers method [33, 34]. In a typical process, 1 g of SiO (2 μm) was dispersed in 150 mL water under stirring for 30 mins.
Then 3g of PDDA (Sigma-Aldrich) was added and the mixture was stirred for another 30 mins. Afterwards, as-prepared GO solution was added dropwise to the PDDA-SiO suspension with a mass ratio of 28:1 between SiO and GO. After 2 h stirring, the GO/PDDA-SiO was obtained by vacuum filtration followed by washing sequentially with water and ethanol, and finally drying in vacuum oven at 80 °C overnight. The GO/PDDA-SiO was then transferred to a horizontal quartz tube. Ar/H₂ (95:5 v/v) was introduced at a flow rate of 1500 sccm for 20 min to purge the system. Afterwards the flow rate was reduced to 100 sccm and the tube was heated to 950 °C with a ramping rate of 10 °C/min and kept for 5 h. The samples were taken out of the tube at temperatures below 40 °C and immersed in 20 wt% HF solution (H₂O: ethanol = 5:1 by volume) at room temperature for 3 h to remove SiO₂. The obtained porous Si was collected by filtration and washed with distilled water and ethanol in sequence several times. The final product was dried in a vacuum oven at 60 °C for 4 h. Carbon coating of G/Si was done by thermal decomposition of acetylene gas at 800 °C for 10 min in a quartz furnace. The mixture of acetylene and high-purity argon (argon: acetylene = 9:1 by volume) is introduced at a flow rate of 100 sccm. Si-C was prepared similarly without the addition of GO.

**Characterization:** The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å). The operating voltage and current were kept at 40 kV and 30 mA, respectively. The size and morphology of the as-synthesized products were determined by a JEOL-1200 transmission electron microscope (TEM), FEI Nova NanoSEM 630 scanning electron microscope (SEM). Raman spectroscopy was conducted with a WITec CMR200 confocal Raman instrument.

**Electrochemical measurements:** Electrochemical experiments were performed using 2016-type coin cells, which were assembled in an argon-filled dry glovebox (MBraun, Inc.) with the G/Si-C and Si-C electrodes as the working electrode and the Li metal as the counter electrode. The working electrodes were prepared by casting the slurry consisting of 80 wt% of active material and 20 wt% of poly(acrylic acid) (PAA) binder. Six different electrode types with different mass loadings of active materials
(around 1.2, 2.0 and 3.2 mg/cm$^2$; see Table 5-1 for details) were fabricated using G/Si-C and Si-C. 1 mol/L LiPF$_6$ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC: DEC: DMC, 2:1:2 by vol. %) and 10 wt% fluoroethylene carbonate (FEC) was used as the electrolyte (Novolyte Technologies, Independence, OH). The electrochemical performance was evaluated by galvanostatic charge/discharge cycling on an Arbin BT-2000 battery tester at room temperature under different current densities in the voltage range between 1 and 0.01 V versus Li$^+$/Li. The current density and specific capacity are calculated based on the mass of the composites.

**Table 5-1. Summary of mass loading and charge/discharge protocol for different G/Si-C and Si-C electrodes**

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Mass loading of active materials (mg/cm$^2$)</th>
<th>Charge/discharge current density (mA/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G/Si-C@low</td>
<td>1.20</td>
<td>400 for the first 2 cycles and 1000 for the following cycles</td>
</tr>
<tr>
<td>G/Si-C@medium</td>
<td>1.98</td>
<td>100 for the first 2 cycles and 600 for the following cycles</td>
</tr>
<tr>
<td>G/Si-C@high</td>
<td>3.18</td>
<td>50 for the first 2 cycles and 400 for the following cycles</td>
</tr>
<tr>
<td>Si-C@low</td>
<td>1.14</td>
<td>400 for the first 2 cycles and 1000 for the following cycles</td>
</tr>
<tr>
<td>Si-C@medium</td>
<td>2.07</td>
<td>100 for the first 2 cycles and 600 for the following cycles</td>
</tr>
<tr>
<td>Si-C@high</td>
<td>3.1</td>
<td>50 for the first 2 cycles and 400 for the following cycles</td>
</tr>
</tbody>
</table>
5.3 Results and Discussion

Figure 5-1. Preparation process of G/Si-C.

Figure 5-1 shows the preparation process of the G/Si-C composite. According to the previous report [35], poly(diallyldimethylammonium chloride) (PDDA) is employed to make a GO/PDDA-SiO assembly, with PDDA acting as a positively charged medium to attract (graphite oxide) GO and SiO, both of which are negatively charged (see Figure 5-2 for more on the influence of PDDA) [35, 36]. The GO/PDDA-SiO assembly is then heated in an H₂/Ar atmosphere. During this process, GO is reduced to graphene and at the same time SiO is disproportionated to Si and SiO₂. After removal of SiO₂ by HF treatment, G/Si is obtained. Finally, carbon filling by decomposition of gaseous carbon precursor leads to formation of G/Si-C, in which both of graphene sheets and porous Si are coated by carbon.
Figure 5-2. Comparison between SiO, GO/SiO and GO/PDDA-SiO in H$_2$O. GO formed stable dispersion without PDDA and no assembly happened between GO and SiO. With addition of PDDA, GO and SiO assembled to leave a transparent aqueous solution, similar to SiO solution.
Figure 5.3. (a) XRD pattern and (b) Raman spectrum of G/Si-C. (c) TEM of GO/PDDA-SiO. (d) Low- and (e) high-magnification TEM images, and (f) SEM image of G/Si-C.
The phase and crystallinity of G/Si-C were investigated by XRD. As shown in Figure 5-3a, the peaks of the pattern can be indexed to those of crystalline face-centered cubic Si (JCPDS Card No.27-1402). Figure 5-3b shows the Raman spectrum of G/Si-C, with peaks at 1333 and 1614 cm\(^{-1}\), corresponding to the D (disordered) band and the G (graphitic) band of carbon, respectively [37]. These two peaks confirm the presence of carbon in the composite. The carbon content was determined by elemental analysis before and after carbon coating to distinguish graphene and carbon from acetylene decomposition. The carbon content is around 30 wt% in total, with 6 wt% and 24 wt% in the form of graphene and carbon from acetylene decomposition, respectively. The intensity of the D band is comparable to that of G band, indicating an overall amorphous carbon structure derived from the majority of the carbon formed by acetylene decomposition.

The morphology, size, and structure of the composite have been investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Figure 5-3c shows a typical TEM image of GO/PDDA-SiO. It is clear that SiO particles are covered by graphene sheets (the edge is marked by white arrows). TEM images of products obtained at different steps are available in Figure 5-4. Similar morphology to these is observed in G/Si-C (Figure 5-3d), which indicates that the assembled graphene/Si structure is preserved during the HF etching and carbon coating processes. The high-magnification TEM image in Figure 5-3e shows that micro-sized particles are composed of interconnected nanoparticles with a size of about 10 to 15 nm. In addition, wrinkles, a characteristic feature of graphene sheets [28, 31, 38, 39], can also be clearly seen (marked by white arrows). Figure 5-3f shows an SEM image of G/Si-C, in which micro-sized particles wrapped by graphene sheets are found, consistent with the TEM observations.
Galvanostatic charge-discharge tests were carried out to evaluate the electrochemical performance. To determine the influence of the incorporation of graphene, Si-C composite with similar carbon content (30 wt%) was also prepared and tested as the control sample. Electrodes with three different active material mass loadings (around 1.2, 2.0 and 3.2 mg/cm$^2$) were fabricated for each composite, and were designated G/Si-C@low, G/Si-C@medium, G/Si-C@high, Si-C@low, Si-C@medium and Si-C@high, where low, medium, and high referred to mass loading. Note that all electrodes were prepared without any external carbon additives (electrodes used only composites and binder in an 8:2 ratio). Considering the potential increase in electrode resistance with increasing mass loading, lower activation current
densities were used for electrodes with medium and high mass loading (see Table 5-1 for details).

Figure 5-5a-d shows cycling performance of G/Si-C and Si-C electrodes with different mass loadings in both gravimetric and areal forms. It is clear that increasing mass loading has no obvious effect on gravimetric capacity of G/Si-C for the initial cycles. All three G/Si-C electrodes exhibit similar gravimetric capacities of about 1100 mAh/g (Figure 5-5a), indicating a similar degree of material utilization. Areal capacity thus increases almost linearly with mass loading. As shown in Figure 5-5b, G/Si-C@low and G/Si-C@medium exhibits about 1.3 and 2.1 mAh/cm², respectively, while G/Si-C@high can deliver an areal capacity of 3.2 mAh/cm² after 100 cycles, comparable to that of commercial LIBs [32]. By contrast, the gravimetric capacity of Si-C is sharply decreased by high mass loading (Figure 5-5c). Although Si-C@low has a similar gravimetric capacity to that of G/Si-C@low, the increase in mass loading dramatically decreases the gravimetric capacity. Si-C@medium shows a low gravimetric capacity of about 740 mAh/g after the initial two cycles, only about 65% of that of Si-C@low. As a result, the areal capacity of Si-C@medium is close to that of Si-C@low (Figure 5-5d). Further increase in mass loading leads to even lower gravimetric capacity. Si-C@high delivers only 580 mAh/g, barely above half that of Si-C@low. This gravimetric capacity drop means that only a slight increase in areal capacity of Si-C, from 1.3 to 1.8 mAh/cm², was achieved when the mass loading was almost tripled. It is also clear that Si-C@high showed capacity fading. We ascribe this to high mass loading and high degree of material utilization. Higher mass loading, generally accompanied by larger volume, results in slow relaxation of stress. Added to this, higher degree of material utilization is directly related to larger volume change, which generates more stress. These two factors together lead to larger stress in the electrode. Further material and electrode optimization such as introducing built-in void into materials and developing new binders may help to stabilize the cyclability.
Figure 5-5. (a-d) cycling performance of G/Si-C and Si-C. First cycle voltage profiles of (e) G/Si-C and (f) Si-C at low and high mass loadings.

Figure 5-5e and f show the first cycle voltage profiles of the extreme cases — G/Si-C and Si-C electrodes with low and high mass loadings. G/Si-C@low delivered charge (delithiation) and discharge (lithiation) capacities of 1314 and 1939 mAh/g, corresponding to a coulombic efficiency (CE) of 67% (Figure 5-5e). A similar...
CE of 64.0% was obtained for G/Si-C@high as 1834 and 2864 mAh/g were achieved (Figure 5-5e). In comparison, the first cycle CE decreased pronouncedly for Si-C at high mass loading. As shown in Figure 5-5f, the charge and discharge capacities of Si-C@low are 1320 and 1950 mAh/g, giving a CE of 68%. However, Si-C@high has a lower CE of 57% with charge and discharge capacities of 1423 and 2471 mAh/g, respectively. Aside from the first cycle CE, another noticeable difference between G/Si-C and Si-C is the lithiation plateau at high mass loading. G/Si-C@high has a lithiation plateau of about 0.15V, higher than 0.11 V of Si-C@high. This is indicative of a lower polarization of the G/Si-C electrode than that of the Si-C one [31]. Such difference is due to the incorporation of graphene sheets as a conductive network [28, 39], which provides additional electron transport pathways between Si-C particles. It is worth noting that the presence of graphene, unlike in many previous reports [40-43], does not significantly decrease the first CE (only from 68% to 67%), which is probably due to the low content of graphene (6 wt%). G/Si-C@high also has high CE after the initial cycle. Figure 5-6a shows the CE from 2nd to 100th cycle, with the red line marking 99.5%. The CE increases above 99.5% in 15 cycles and remains that high afterwards. The average CE from the 2nd to 100th cycle is 99.57%, which is rarely reported for Si-based electrodes with high mass loading.

![Figure 5-6](image_url)

*Figure 5-6.* (a) Coulombic efficiency (2nd to 100th cycle) of G/Si-C@high. (b) Impedance spectra of G/Si-C and Si-C at low and high mass loadings. Insets in (b) are the Randles equivalent circuit and enlarged spectra showing difference between G/Si-C@low and G/Si-C@high, respectively.
The difference in electrochemical performance was further studied by electrochemical impedance spectroscopy (EIS) measurements. Figure 5-6b shows the Nyquist plots of G/Si-C and Si-C electrodes with low and high mass loadings, as two extremes, after five cycles at delithiated state. All spectra consist of a depressed semicircle in the high-to-medium frequency range and a straight line in the low frequency range. The Randles equivalent circuit (upper inset) was employed to analyze the impedance spectra [31]. According to the fitting results (Table 5-2), the charge transfer resistance of G/Si-C@high is 10.9 Ω, similar to that of G/Si-C@low (9.14 Ω, middle inset). By contrast, Si-C@high has a much higher charge transfer resistance of 59.98 Ω than Si-C@low (16.83 Ω). The difference in resistance, especially at high mass loading, serves strong evidence of improvement in electronic conductivity through forming conductive network by graphene at both low and high mass loadings.

**Table 5-2.** Parameters of equivalent electrical circuits corresponding to Nyquist plots of four different electrodes in Figure 5-6b

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Rs(Ω)</th>
<th>Rct(Ω)</th>
<th>CPE-T(F)</th>
<th>CPE-P</th>
<th>W₀-R(Ω)</th>
<th>W₀-T(s)</th>
<th>W₀-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>G/Si-C@low</td>
<td>2.64</td>
<td>9.14</td>
<td>3.6 x10⁻⁵</td>
<td>0.7512</td>
<td>21.26</td>
<td>0.821</td>
<td>0.18</td>
</tr>
<tr>
<td>G/Si-C@high</td>
<td>2.74</td>
<td>10.90</td>
<td>4.6 x10⁻⁵</td>
<td>0.73</td>
<td>23.12</td>
<td>1.269</td>
<td>0.16</td>
</tr>
<tr>
<td>Si-C@low</td>
<td>3.74</td>
<td>16.83</td>
<td>5.9 x10⁻⁵</td>
<td>0.87</td>
<td>67.61</td>
<td>6.330</td>
<td>0.31</td>
</tr>
<tr>
<td>Si-C@high</td>
<td>3.32</td>
<td>59.98</td>
<td>1.0x10⁻⁵</td>
<td>0.7664</td>
<td>76.92</td>
<td>8.173</td>
<td>0.56</td>
</tr>
</tbody>
</table>
To better understand the reason for the high degree of material utilization, post-cycling SEM and TEM investigation was carried out on delithiated Si-C@high electrode after 100 cycles. Acetonitrile and 1 M hydrochloric acid solution were used to remove electrolyte, SEI layer, and binder of the TEM sample. As shown in Figure 5-7a, the structure of electrode maintains well as only small cracks are present without any active material peeling off, similar to our previous report [23]. TEM observation (Figure 5-7b) reveals change of the active material at nanoscale level. The micro-sized composite did break into smaller pieces during cycling. However, these pieces were still connected by graphene sheets, similar to the structure before cycling (Figure 5-3d), which effectively decreased the contact resistance between smaller pieces and thus ensured good material utilization.

5.4 Conclusion

In summary, a graphene-wrapped micro-sized Si-C composite has successfully been prepared via a facile approach. The graphene provides additional electron pathways for the whole electrode by forming a conductive network that connects different Si-C particles, giving the G/Si-C conductive networks both within and between particles. As a result, low electrical resistance can be maintained at high mass loading, which enables a high degree of material utilization. Correspondingly,
the graphene-wrapped Si-C composite exhibits a high areal capacity of 3.2 mAh/cm$^2$ after 100 cycles with high coulombic efficiency. These findings demonstrate the importance of building a conductive network at the electrode level for high material utilization at high mass loading and may shed light on future designs of Si-based anodes with high areal capacity.
Reference


Chapter 6: High-Performance Hybrid Battery Enabled by a High-Rate Si-Based Anode

6.1 Introduction

The expanding market of portable electronic devices and, especially, the emergence of electric vehicles (EV) and hybrid electric vehicles (HEV) have created increasing demand for advanced energy storage techniques that can provide high energy and power densities and long cycling life.\(^{[1, 2]}\) In today’s practical applications, the two major energy storage systems are lithium-ion batteries (LIBs) and supercapacitors (SCs), which represent two extremes of the design space. LIBs can deliver high energy densities (150–250 Wh/kg) by utilizing Faradaic reactions throughout the active materials.\(^{[3]}\) However, this mechanism leads to low power densities (<1000 W/kg) since solid-state ion diffusion in bulk electrodes is generally slow.\(^{[3, 4]}\) LIBs also suffer from short cycling lives (<1000 cycles) due to degradation of material structures.\(^{[5]}\) On the opposite extreme, SCs offer high power densities (~10,000 W/kg) because of the fast physical sorption rates of charges on the surfaces of active materials.\(^{[3, 6]}\) This mechanism also enables long cycling lives (>100,000 cycles), since it does not cause major structural changes.\(^{[7]}\) However, as only the surface is utilized, the energy densities of SCs are very limited (5-10 Wh/kg).\(^{[7, 8]}\) In view of issues of current LIBs and SCs, it is highly desirable, but also very challenging, to develop an energy storage system with high energy and power densities and long cycling life by combining the advantages of both LIBs and SCs.
Figure 6-1. Charging process of a hybrid battery using activated carbon as the cathode and a Li-insertion material as the anode.

Li-ion hybrid batteries or supercapacitor–battery hybrid energy storage systems have been proposed as a way to incorporate the advantages of both LIBs and SCs into one system.\(^9\)\(^-\)\(^11\) Such systems usually consist of SC electrodes (activated carbon) as cathodes to ensure high power density through adsorption/desorption of anions and LIB electrodes as anodes to provide high energy density by lithium insertion/extraction in a non-aqueous electrolyte (Figure 6-1).\(^12\) Various examples of such systems have been reported with encouraging results.\(^5\), \(^9\)\(^-\)\(^11\), \(^13\)-\(^17\) For example, Zhang et al. demonstrated the highest energy density to date (147 Wh/kg at 150 W/kg) by coupling a graphene-based three-dimensional porous carbon cathode and a Fe\(_3\)O\(_4\)/graphene nanocomposite anode.\(^13\) However, in most of these reports, high energy densities are only achieved at very low power densities, and energy densities decrease significantly with increasing power densities. A system with high energy density at high power density, along with long cycling life, has not yet been demonstrated. This is largely due to a lack of high performance anodes. Assuming a
strictly linear charge/discharge slope without voltage drop, the energy and power densities can be calculated by the following equations:

\[ E = \frac{1}{2} (V_1 + V_2) I \Delta t \]  

(1)

\[ P = \frac{E}{\Delta t} \]  

(2)

where \( E, P, V_1, V_2, I, \) and \( \Delta t \) are the energy density, power density, lower and upper limits of the voltage window, current density, and discharge duration, respectively.\(^{15, 18}\)

According to these equations, to achieve high energy and power densities requires high operating voltage \((V_1+V_2)\), high rate capability (which allows for high current density), and high capacity (which gives long discharge duration). Because the anode undergoes lithiation during charging of the hybrid battery, a lower anode lithiation voltage enables a higher \( V_2 \) and thus leads to higher energy and power densities if other parameters are unchanged. In addition, good anode cycling stability is indispensable for long cycling life of the hybrid batteries, since Faradaic anodes usually suffer from shorter cycling lives compared to capacitive cathodes. Based on the analysis above, an ideal anode in a hybrid battery system should have the following features: 1) the working voltage should be low so that the system is able to fully utilize the voltage window of the electrolyte to enable high energy density; 2) the anode should have high specific capacity to increase the energy density; 3) the anode should have excellent rate capability to match the high-power cathode to achieve high power density; 4) the cycling life should be long to improve cycling stability of the hybrid system. However, none of the anode materials used thus far in hybrid batteries meets all these requirements. For example, \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and \( \text{TiO}_2 \) have good cycling stability but high voltage (1.5 V) and low capacity (around 200 mAh/g).\(^{4, 8}\) Graphite, on the other hand, shows the lowest lithiation voltage (0.1 V) but low capacity (370 mAh/g) and mediocre rate performance.\(^{6}\)

Silicon is a promising anode material candidate for hybrid batteries because of its low lithiation potential (<0.5 V) and high specific capacity (>3500 mAh/g).\(^{19, 20}\) However, Si suffers from fast capacity fading caused by its large volume change.
(>300%) during lithiation/delithiation. In addition, Si has low electronic conductivity due to its intrinsic semiconductor nature, which limits its rate capability. Thus, preparing Si-based anodes with long cycling life and high power density is an essential requirement for Si-containing hybrid batteries. Tremendous efforts have been made to solve these issues of Si-based anodes, frequently by designing Si nanostructures such as nanowires, nanotubes, nano and micro-sized particles. However, preparation of most of these materials involves costly chemical/physical vapor deposition or highly toxic hydrofluoric acid (HF) etching. Herein, we report a hybrid battery with high energy and power densities enabled by a high-performance Si-based anode. The cycling stability and rate performance of the anode material were improved by size reduction, carbon coating, and boron doping of commercial silicon monoxide (SiO) without any HF etching. When used as a Li-ion battery anode, the resultant composite (B-Si/SiO₂/C) exhibits a capacity of 1279 mAh/g after 100 cycles at 0.6 A/g (92.7% capacity retention) and excellent high rate performance of 685 mAh/g at 6.4 A/g. Coupling this material with highly porous carbon (PSC) creates a high-voltage hybrid battery (B-Si/SiO₂/C//PSC) operating between 2.0-4.5 V with a high energy density of 128 Wh/kg at 1229 W/kg. Even at a high power density of 9704 W/kg, 89 Wh/kg can be retained, the highest values of any hybrid battery to date. In addition, the hybrid battery shows good capacity retention of 70% after 6000 cycles at 1.6 A/g and a low self-discharge rate with voltage retention of 82% after 50 hours.

6.2 Experimental Section

Synthesis of boron-doped Si/SiO₂/C composite: Commercially available SiO powder (325 mesh) from Aldrich was used as precursor. For size reduction, SiO powder was subject to planetary ball-milling for 12 h at a speed of 400 rpm. The boron-doping was carried out in a horizontal quartz tube. A mixture of SiO powder (325 mesh, Sigma Aldrich) and B₂O₃ powder (Alfa Aesar) with 20:1 molar ratio of Si:B was used as the starting material. In a typical process, high-purity Ar was introduced at a flow
rate of 1500 sccm for 20 min to purge the system. Afterwards the flow rate was reduced to 100 sccm and the tube was heated to 950 °C with a ramping rate of 10 °C/min, and kept at 950 °C for 5 h. The samples were taken out of the tube at temperatures below 40 °C. Carbon coating was done by thermal decomposition of acetylene gas at 700 °C for 30 min in a quartz furnace. The mixture of acetylene and high-purity argon (argon: acetylene = 9:1 by volume) is introduced at a flow rate of 100 sccm.

*Synthesis of PSC Microspheres:* PSC microspheres were prepared according to our previous report.[36]

*Characterization:* The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å). The operating voltage and current were kept at 40 kV and 30 mA, respectively. The size and morphology of the as-synthesized products were determined by a JEOL-1200 transmission electron microscope (TEM), FEI Nova NanoSEM 630 scanning electron microscope (SEM) and JEOL-2010F high-resolution transmission electron microscope (HRTEM). X-ray photoelectron spectroscopy (XPS) was conducted with a Kratos Analytical Axis Ultra XPS. Raman spectroscopy was conducted with a WITec CMR200.

*Electrochemical measurements:* The electrochemical experiments were performed using 2016-type coin cells, which were assembled in an argon-filled dry glovebox (MBraun, Inc.). For half-cell testing, PSC and B-Si/SiO₂/C electrodes were used as the working electrodes and the Li metal was used as the counter and reference electrode. PSC electrodes were prepared by casting a slurry consisting of 80 wt% of active material, 10 wt% of Super P carbon black, and 10 wt% of polyvinylidene fluoride (PVDF) binder on carbon-coated aluminum foil. B-Si/SiO₂/C electrodes were prepared by mixing 70 wt% of active material, 15 wt% of Super P carbon black, and 15 wt% of poly(acrylic acid) (PAA) binder. 1 mol/L LiPF₆ in a mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC: DEC: DMC, 2:1:2 by vol.) and 10 wt% fluoroethylene carbonate (FEC) was used as the electrolyte (Novolyte Technologies, Independence, OH). The hybrid battery was fabricated by coupling a
prelithiated B-Si/SiO₂/C electrode (cycled 10 times, ending in a lithiated state at 0.2 V) and a fresh PSC electrode. The mass ratio of PSC to B-Si/SiO₂/C is 2:1. The mass loadings of active materials in the cathode and anode electrodes are 4 and 2 mg/cm², respectively. The electrochemical performance was evaluated by galvanostatic charge/discharge cycling on an Arbin BT-2000 battery tester at room temperature under different current densities. The voltage ranges for the PSC electrode and the B-Si/SiO₂/C electrode were 2.0-4.5 V and 0.01-1.5 V versus Li⁺/Li, respectively. The hybrid battery was measured in the voltage range between 2.0 and 4.5 V versus Li⁺/Li. The current density was calculated based on the total mass of active materials on both the cathode and the anode. Cyclic voltammetry (CV) measurements were carried out on a Solartron SI 1287 electrochemical interface. Electrochemical impedance spectroscopy (EIS) was carried out by applying a perturbation voltage of 5 mV between 10 mHz and 100 kHz using a Solartron SI 1260 impedance analyzer. The energy density (E) and power density (P) of the hybrid battery were calculated according to the following equations:

\[ E = \int_{t_1}^{t_2} IV \, dt \]  \hspace{1cm} (1)

\[ P = \frac{E}{t_2 - t_1} \]  \hspace{1cm} (2)

where \( E \) (Wh/kg), \( V \) (V), \( I \) (A/kg), \( t_1 \) and \( t_2 \) (h) and \( P \) (W/kg) are the energy density, voltage, constant current density, discharge start and end time, and power density, respectively.
6.3 Results and Discussion

Figure 6-2. (a) XRD patterns of B-Si/SiO$_2$/C and Si/SiO$_2$/C. (b) B 1s XPS spectrum, (c) Raman spectrum and (d) SEM image of B-Si/SiO$_2$/C. (e) HRTEM image of B-Si/SiO$_2$. (f) TEM image of B-Si/SiO$_2$/C.
Figure 6-2a shows the X-ray diffraction (XRD) patterns of B-Si/SiO$_2$/C and Si/SiO$_2$/C. Both patterns contain the peaks associated with crystalline Si (JCPDS Card No.27-1402) and amorphous SiO$_2$, formed by disproportionation of SiO during heat treatment of the samples.$^{[30]}$ The average size of Si nanocrystallites in both samples is estimated to be about 15 nm by the Debye–Scherrer equation. However, careful observation reveals a slight difference of Si peak positions between the two samples. The Si peaks of B-Si/SiO$_2$/C are at higher angles than those of Si/SiO$_2$/C due to the B-doped material having smaller lattice constants, indicating the replacement of Si atoms by smaller B atoms.$^{[31, 32]}$ In addition, no peaks of Si–B alloy are observed, supporting that B is doped into the Si. The boron doping was further examined by X-ray photoelectron spectroscopy (XPS). As shown in Figure 6-2b, both a B–O peak (193 eV) and a weak B–B/B–Si peak (188/187 eV) are present, agreeing well with the previous study on B-doped Si nanocrystals embedded in a silicon dioxide matrix and serving as solid evidence of boron doping.$^{[33]}$ The content of B is calculated to be around 4% (atomic percentage) by XPS survey. Raman spectroscopy (Figure 6-2c) of B-Si/SiO$_2$/C shows two peaks at 1340 and 1605 cm$^{-1}$ that are attributed to the D (disordered) band and the G (graphite) band of carbon, indicating the presence of carbon formed by thermal decomposition of acetylene.$^{[28]}$ The mass percentage of carbon in B-Si/SiO$_2$/C was found to be 3.5% by elemental analysis.

Figure 6-3. Comparison by SEM of (a) B-Si/SiO$_2$/C and (b) B-Si/SiO$_2$/C-325.
The morphology, size, and structure of B-Si/SiO₂/C were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in the SEM image (Figure 6-2d), B-Si/SiO₂/C is composed of micro-sized particles with an average size of about 3 μm and sub-micron particles, much smaller than the size (20 μm, Figure 6-3) of the pristine SiO precursor before ball milling. The nanoscale structure of disproportionated SiO is shown in the high-resolution TEM (HRTEM) image (Figure 6-2e). Lattice fringes with a d-spacing of 0.31 nm can clearly be seen, corresponding to the (111) crystal planes of the Si. It is also clear that crystalline Si domains with size of around 15 nm are dispersed in an amorphous SiO₂ matrix, the latter of which could act as a buffer layer for volume change of Si during lithiation/delithiation and thus improve cycling stability. Figure 6-2f shows the TEM image of B-Si/SiO₂/C, in which the thickness of the carbon layer (marked by white arrows) was found to be around 20-30 nm. A low-magnification TEM showing overall morphology with the carbon layer is available in Figure 6-4.

Figure 6-4. Low-magnification TEM of B-Si/SiO₂/C showing a carbon coating layer.
The influence of size reduction of the SiO precursor and boron doping on the electrochemical performance of the resultant products was evaluated by galvanostatic cycling in Li-ion half-cells. For comparison, boron-doped Si/SiO$_2$/C using SiO which was not ball-milled (B-Si/SiO$_2$/C-325) and undoped Si/SiO$_2$/C using ball-milled SiO (Si/SiO$_2$/C) were prepared. These control samples have similar carbon content (3.5 wt%) to B-Si/SiO$_2$/C. Figure 6-5a shows the cycling performance of B-Si/SiO$_2$/C and B-Si/SiO$_2$/C-325 at a current density of 600 mA/g with the first two cycles activated at 300 mA/g. It is clear that B-Si/SiO$_2$/C exhibits better cycling stability than B-Si/SiO$_2$/C-325. A capacity of 1279 mAh/g was obtained by B-Si/SiO$_2$/C after 100 cycles, equating to 92.7% capacity retention (based on the lithiation capacity of the 3rd cycle), while B-Si/SiO$_2$/C-325 only delivered 990 mAh/g after 100 cycles, only 75% of its initial capacity. B-Si/SiO$_2$/C also has higher specific capacity during its first several cycles than B-Si/SiO$_2$/C-325, indicating that size reduction leads to short charge transport paths and thus increased material utilization. Another notable feature of B-Si/SiO$_2$/C is its high coulombic efficiency (CE) during cycling. B-Si/SiO$_2$/C shows an acceptable first cycle CE of 71%. The CE quickly rises to 99.5% and 99.7% after 9 and 20 cycles, respectively, and thereafter remains at that level. The average CE from the 2nd to 100th cycle is 99.67%, which is rarely reported for Si-based anode materials. The doping effects on reduced-size Si/SiO$_2$/C were examined by charge/discharge at different current densities. As shown in Figure 6-5b, the difference in the specific capacities of doped and undoped ball-milled Si/SiO$_2$/C becomes more and more pronounced with increasing current density. At a high current density of 6.4 A/g, B-Si/SiO$_2$/C delivers a capacity of 685 mAh/g, 2.4 times that of Si/SiO$_2$/C (286 mAh/g). After the current density was restored to 400 mA/g, B-Si/SiO$_2$/C showed excellent reversibility, with a capacity similar to its initial capacity, while Si/SiO$_2$/C showed lower capacity and poor stability. The improved rate performance by boron doping is ascribed to a lower charge transfer resistance, as evidenced by electrochemical impedance spectroscopy (EIS) (Figure 6-6). The B-Si/SiO$_2$/C has a smaller semicircle in the high-to-medium frequency region, which is generally ascribed to having a lower charge transfer resistance. It is worth noting
that the CE of B-Si/SiO$_2$/C remains around 99.7% even at high rates. Figure 6-5c shows voltage profiles of B-Si/SiO$_2$/C at different rates. A relatively flat lithiation plateau below 0.3 V can be observed in all profiles. A large portion of capacity is reserved even under lower voltage, for example, 0.2 V as marked by dash line. As an extreme, the capacity is 108 mAh/g when B-Si/SiO$_2$/C was lithiated to 0.2 V at 6.4 A/g, giving 577 mAh/g that could be used when lithiated B-Si/SiO$_2$/C is coupled as an anode in a hybrid battery. The large capacity reservoir at high current density, combined with the low voltage plateau, should enable a large voltage window in a hybrid battery.

**Figure 6-5.** (a) Cycling performance of B-Si/SiO$_2$/C and B-Si/SiO$_2$/C-325 at 600 mA/g, after the first two cycles of activation at 300 mA/g. (b) Rate performance of B-Si/SiO$_2$/C and Si/SiO$_2$/C. Voltage profiles of (c) B-Si/SiO$_2$/C and (d) PSC at different current densities. Data are from tests in half-cell configuration with Li foil as counter electrodes.
Porous spherical carbon (PSC), which was reported in our previous work on lithium-sulfur batteries, was chosen as the cathode material. The physical properties of PSC have been well characterized, featuring a hierarchical mesoporous structure with mesopores ranging from 5 to 25 nm in diameter, a high surface area of 1014 m²/g, and a high pore volume of 2.5 cm³/g. The PSC was evaluated in a Li half-cell over a potential range of 2.0 to 4.6 V (Figure 6-5d). Capacities vary from 65 to 55 mAh/g at 0.8-6.4 A/g. Linear charge/discharge profiles were observed at all current densities, indicating capacitive behavior with the adsorption/desorption of ions on the surface. The cyclic voltammetry (CV) curves (Figure 6-7) also show quasi-rectangular shapes, close to the ideal capacitive behavior.
Based on the electrochemical characteristics of B-Si/SiO$_2$/C and PSC, the following guidelines were used for design and evaluation of the hybrid battery. B-Si/SiO$_2$/C was cycled 10 times at 400 mAh/g in a Li half-cell to achieve high efficiency and then lithiated to 0.2 V. Thereafter the lithiated B-Si/SiO$_2$/C electrode was coupled with a fresh PSC cathode to fabricate a hybrid battery (B-Si/SiO$_2$/C//PSC). The mass ratio of PSC to B-Si/SiO$_2$/C was set at 2:1 to obtain long cycling life, as this left a fair margin of anode for gradual consumption of Si due to structural degradation during extended cycling.\textsuperscript{[29]} The voltage window of 2.0–4.5 V was chosen to avoid both oxidative decomposition of electrolytes and possible Li intercalation into the carbon-based cathode (under 2.0 V, Figure 6-8).\textsuperscript{[37, 38]}

**Figure 6-7.** CV curves of PSC from 2 to 4.6 V in a Li half-cell.
Figure 6-8. Galvanostatic charge–discharge curves of B-Si/SiO$_2$/C//PSC hybrid battery from 1.5 to 4.0 V showing a plateau from 1.7 to 1.5 V marked by the red box, which is attributed to intercalation of Li to non-graphitic carbon.
The CV curves of the hybrid battery from 2.0 to 4.5 V are shown in Figure 6-9a. As the scan rate increased, the curves gradually deviated from the ideal rectangular shape due to the overlapping effects of capacitive behavior from the cathode and Faradaic behavior from anode. Figure 6-9b shows the voltage profiles at different current densities. Note that the current densities are based on the total mass of active material on both the cathode and the anode. The curves show little deviation from the linear slope of an ideal supercapacitor, which is due to the relatively flat charge/discharge plateau of the Si-based anode. The energy and power densities of the hybrid battery were calculated based on these curves and the results are shown in Figure 6-9c in comparison with energy densities at maximum power densities of each previous study. A high energy density of 128 Wh/kg can be achieved at a power density of 1229 W/kg. Even at an ultra-high power density of 9704 W/kg, which is on a par with conventional supercapacitors, the hybrid battery can still deliver 89 Wh/kg. To the best of our knowledge, such high energy and power densities have not been achieved by other hybrid battery systems. Given that the mass percentage of active materials in commercial energy storage devices is about 35-40%,\textsuperscript{[39]} the gravimetric energy density of a device using this B-Si/SiO\textsubscript{2}/C//PSC system could reach 32 Wh/kg at 3396 W/kg. In addition, such a device could have high volumetric energy and power densities thanks to the high tap densities of both PSC (0.5 g/cm\textsuperscript{3}) and
B-Si/SiO$_2$/C (0.7 g/cm$^3$), which stem from their micron-scale particle size. Finally, one key advantage of supercapacitors over other energy storage techniques is their long-term cycling stability.$^{[7]}$ Figure 6-9d shows the cycling performance of the hybrid battery at 1.6 A/g. The capacity retention is 70% after 6000 cycles. The influence of voltage window on the performance of the hybrid battery was investigated. A drop of 0.5 V in upper limit voltage (2.0 to 4.0 V) slightly decreases power densities but nearly halves energy densities while improves the cycling performance with a capacity retention of 77% after 6000 cycles (Figure 6-10 and Table 6-1). These results clearly show the importance of high upper limit voltage in improving energy densities of hybrid batteries.

![Figure 6-10](image-url)

**Figure 6-10.** Performance of the B-Si/SiO$_2$/C//PSC hybrid battery with a voltage window from 2.0 to 4.0 V. (a) galvanostatic charge–discharge curves, (b) Ragone plot in comparison with energy and power densities from 2.0 to 4.5 V, and (c) cycling performance.
Table 6-1. Power and energy densities of the B-Si/SiO$_2$/C//PSC hybrid battery obtained with different voltage windows

<table>
<thead>
<tr>
<th>Current density (A/g)</th>
<th>0.4</th>
<th>0.8</th>
<th>1.6</th>
<th>3.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power density (W/kg)</td>
<td>2.0-4.5 V</td>
<td>1229</td>
<td>2473</td>
<td>4925</td>
</tr>
<tr>
<td></td>
<td>2.0-4.0 V</td>
<td>1200</td>
<td>2388</td>
<td>4736</td>
</tr>
<tr>
<td>Energy density (Wh/kg)</td>
<td>2.0-4.5 V</td>
<td>128</td>
<td>115</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>2.0-4.0 V</td>
<td>64</td>
<td>60</td>
<td>56</td>
</tr>
</tbody>
</table>

The self-discharge behavior of supercapacitors is one key concern for practical applications. Conventional supercapacitors suffer from a higher self-discharge rate than Li-ion batteries.$^{[40, 41]}$ Incorporation of a Li-active anode in the hybrid battery was found to reduce the self-discharge rate. The hybrid battery was charged to 4.0 V at 100 mA/g, further charged at a constant potential of 4.0 V for 1 h, and then allowed to undergo self-discharge, all at room temperature. The open circuit voltage as a function of time was measured and is shown in Figure 6-11. The voltage dropped to 3.28 V over 50 hours with a faster rate at the beginning, corresponding to 18% decay. This is much lower than those of the commercial high-voltage (3.5 V) supercapacitor (50% over 8 hours) and the novel graphene-based micro-supercapacitors recently reported (50% over 13 hours).$^{[42]}$
Figure 6-11. Self-discharge curve of the B-Si/SiO$_2$/C//PSC hybrid battery charged to 4.0 V at 100 mA/g followed by constant-voltage charging at 4.0 V for 1 hour at room temperature.

6.4 Conclusion

In summary, we have designed a hybrid battery by coupling a porous carbon cathode and a high-performance Si-based anode. The Si-based anode has good cycling stability and rate performance, delivering a capacity of 685 mAh/g even at a high rate of 6.4 A/g. In addition, the low working voltage of Si grants the hybrid battery a high voltage window of 2.0-4.5 V. As a result, the hybrid battery exhibits a high energy density of 128 Wh/kg at 1229 W/kg. Even when power density increases to the level of a conventional supercapacitor (9704 W/kg), 89 Wh/kg can be obtained. Moreover, this system can achieve a long cycling life, with 70% capacity retention after 6000 cycles. The hybrid battery also features a low self-discharge rate, with voltage retention of 82% after 50 hours. The present findings demonstrate that incorporating high-performance Si-based anodes is an effective approach to boost the energy and power densities of hybrid batteries.
Reference


Chapter 7: Conclusions

With high energy density and long cycle life, lithium-ion batteries (LIBs) are an attractive energy storage system and have been widely used in various portable electronic devices. However, great challenge facing LIBs need to be addressed to achieve their expected application for electric vehicles and stationary energy storage systems. Of particular interest is increasing energy and power densities, lowering cost and improving safety of LIBs. In this dissertation, a series of micro-sized silicon-carbon (Si-C) composites were developed as anode materials for LIBs high energy and power densities and the mechanism behind the electrochemical performance have been investigated.

In Chapter 2, a facile route was developed to produce a micro-sized Si-C composite composed of interconnected Si and carbon nanoscale building blocks. The micro-sized Si-C composite particles consist of nano-sized Si and C that are three-dimensionally interconnected at the nanoscale throughout the particles. A capacity of 1459 mAh/g after 200 cycles at a higher current density of 1A/g and excellent capacity retention of 97.8% were attained. Specific capacities of 110 and 700 mAh/g can be achieved at high current densities of 6.4 A/g and 12.8 A/g, almost 3 times and 2 times the theoretical capacity of graphite, respectively. The volumetric capacity of the micro-sized Si-C composite is calculated to be 1326 mAh/cm³ at 400 mA/g, which is mainly due to the high tap density of the micro-sized Si-C composite (0.78 g/cm³). The excellent performance of the Si-C composite combined with its low-cost and large-scale synthesis makes it a promising anode material for practical application in LIBs.

In Chapter 3, the influence of the Si building block size on the performance of micro-sized Si-C composites and the role that carbon coating temperature plays in improving the performance of the composite with the optimized building block size were investigated. It has been found that the 1st cycle coulombic efficiency and reversible capacity of the Si-C composites increase as building block size increases,
while cycling stability plummets. 15 nm is found to be the critical Si building block size, striking a delicate balance between cycling stability and reversible capacity. On the other hand, the 1st cycle CE and high rate performance can be greatly improved by carbon coating at a higher temperature of 800 °C as more SiO\(_x\) (0<x<2) is reduced and carbon of better quality is formed. Combining the optimized nanoscale building blocks and carbon coating, the resultant composite can sustain 600 cycles at 1.2 A/g with a fixed lithiation capacity of 1200 mAh/g.

In Chapter 4, a novel strategy was developed to enhance the rate capability of Si-C composite by facile boron doping. Boron doping was confirmed by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The boron-doped Si-C composite shows much improved rate capability, delivering a capacity of 575 mAh/g at 6.4 A/g without any external carbon additive, 80% higher than that of undoped composite. The improved rate capability is attributed to lower charge transfer resistance of B-doped Si-C, as shown by EIS measurement. The finding demonstrates that boron doping is an effective approach to enhance rate capability of Si-based anodes for LIBs.

In Chapter 5, a graphene-wrapped micro-sized Si-C composite was prepared via a facile approach to achieve high areal capacities at electrode level. In the composite, micro-sized Si-C particles are wrapped by graphene sheets. The two-dimensional conductive graphene sheets act as a conductive network between particles and thus decrease the contact resistance of the whole electrode. Low electrical resistance can thus be maintained at high mass loading, which enables a high degree of material utilization. Correspondingly, the graphene-wrapped Si-C composite exhibits a high areal capacity of 3.2 mAh/cm\(^2\) after 100 cycles with high cycling coulombic efficiency. The findings demonstrate the importance of building a conductive network at the electrode level to ensure high material utilization at high mass loading and may shed light on future designs of Si-based anodes with high areal capacity.

In Chapter 6, a high-performance micro-sized Si-based material (B-Si/SiO\(_2\)/C) was developed and used to enable a hybrid battery with high energy and power
densities by paring a porous carbon cathode. The cycling stability and rate performance of B-Si/SiO₂/C were improved by size reduction, carbon coating, and boron doping of commercial silicon monoxide (SiO) without any HF etching. B-Si/SiO₂/C exhibits a capacity of 1279 mAh/g after 100 cycles at 0.6 A/g (92.7% capacity retention) and excellent high rate performance of 685 mAh/g at 6.4 A/g. The hybrid battery exhibits a high energy density of 128 Wh/kg at 1229 W/kg. Even at a high power density of 9704 W/kg, 89 Wh/kg can be retained, the highest values of any hybrid battery to date. In addition, the hybrid battery shows good capacity retention of 70% after 6000 cycles at 1.6 A/g and a low self-discharge rate with voltage retention of 82% after 50 hours. This work opens an avenue for development of high-performance hybrid batteries using high-performance Si-based anodes.
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