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Silicon Li-ion Anode Materials via Spray Drying and Magnesiothermic Reduction

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Zheng Yan

June 2019

Dissertation Committee:

Dr. Juchen Guo, Chairperson

Dr. Ruoxue Yan

Dr. Yadong Yin

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2019

The Dissertation of Zheng Yan is approved:

Committee Chairperson

University of California, Riverside

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Dedication

I dedicate this to my parents Xiaomei Zheng and Jun Yan for their love, dedication and enduring encouragement.

This dissertation has used paragraphs, sentences, figures and tables from two pending publication articles by Zheng Yan and Dr. Juchen Guo.

ABSTRACT OF THE DISSERTATION

Silicon Li-Ion Anode Materials via Spray Drying and Magnesiothermic Reduction

by

Zheng Yan

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, June 2019
Dr. Juchen Guo, Chairperson

Silicon (Si) is a high-capacity anode material that can be used to replace or be added in the graphite anode in the next generation lithium-ion (Li-ion) batteries. Tremendous research and development efforts from both academic and industrial sectors are devoted to commercializing Si-based anode materials in the near future, however, successful cases of Si-anode commercialization are still lacking. The technical challenges are most originated from two fundamental properties of Si as a Li storage material: inevitable volume change during lithiation-delithiation and inferior electronic conductivity comparing to graphite. The former results to continuous degradation of the electronic connection in the electrodes and continuous rapture of the solid electrolyte interphase (SEI); the latter seriously limits the areal loading of the Si-based materials in the electrode thus difficult to achieve practical

high-capacity. In addition to the challenges from the material properties, the industrial production process is equally or more important to the commercialization of Si-based anode materials. Such a production process not only must be scalable with economic feasibility feasible but also technologically robust to achieve optimal properties of the Si anode materials.

Among the numerous production methods reported to date, magnesiothermic reduction reaction (MRR) remains a viable candidate for Si material production process. Since Bao and co-workers reported Si synthesis via thermal reduction of silicon oxide by magnesium (Mg), many studies on Si-based anode materials from MRR has been reported. However, there remains some challenges: Due to the exothermic nature of MRR, it is difficult to control the microstructure of the obtained Si due to the fusing of Si. Generation of byproducts magnesium silicate (Mg_2SiO_4) or magnesium silicide (Mg_2Si) is another severe challenge of MRR. These byproducts are induced due to discrepant atoms mobilities in Si-Mg-O system and the chemical stability of the interface between MgO, SiO_2 and Si. Finally, the kinetics of MRR is not well understood therefore it has been difficult to optimize the MRR process.

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Chapter 1: Introduction

1.1 Background

Battery is an energy storage device which converting electricity energy into chemical energy and storing in negative and positive electrode. The invention of Li-ion rechargeable battery enables many revolutions in customer electronics, Electric vehicles, wearables and renewable energy storage applications. Rechargeable Li-ion battery with its low toxicity more environmentally friendly than lead acid batteries or nickel-cadmium batteries. The High energy density, long cycle life and minimal self-discharge rate could beat many technologies such as lead acid, nickel-cadmium and nickel-metal-hybride. The demand for sustainable and clean energy storage materials is becoming more critical due to the tremendous new technologies such as laptop computers, smart phones and electric vehicles (EVs).¹ Handheld electronics mostly use lithium-ion batteries (LIBs) based on lithium cobalt oxide (LiCoO_2).² Lithium iron phosphate (LiFePO_4),³ Lithium manganese oxide (LiMn_2O_4)⁴ cathode LIBs offer relatively lower energy density, but longer lives and inherent safety. Lithium nickel manganese cobalt oxide (LiNiMnCoO_2 or NMC).⁵ represents the state-of-the-art cathode material, which has the highest Li storage capacity. The variation of NMC, lithium nickel cobalt aluminum oxide (LiNiCoAlO_2 or NCA)⁶ is

another high-capacity cathode available on the market. The specifications of current technologies are listed in

Table 1.1. Nowadays, the current technologies of cathode materials have been developed extensively. But the anode materials still mainly focus on graphite.

Table 1.1 current technologies of Li-ion batteries.

Anode material	Cathode materials	Voltage (Nominal)	Capacity	Characteristics
Graphite Capacity: 372 mAh/g	lithium cobalt oxide (LiCoO ₂) Capacity: 140 mAh/g	~3.6 V	150–200Wh/kg	High specific energy; limited specific power; expensive material (cobalt).
	Lithium manganese oxide (LiMn ₂ O ₄) Capacity: 110 mAh/g	~3.8 V	100–150Wh/kg	High power but less capacity; safer than Li-cobalt.
	Lithium iron phosphate (LiFePO ₄) Capacity: 160 mAh/g	~3.3 V	90–120Wh/kg	Very flat voltage discharge curve but low capacity, high power; safest Li-ion batteries
	lithium nickel manganese cobalt oxide (LiNiMnCoO ₂) Capacity: 165 mAh/g	~3.7 V	150–220Wh/kg	High capacity and high power; favorite chemistry for many uses; market share is increasing
	Lithium nickel cobalt aluminum oxide (LiNiCoAlO ₂) Capacity: 190 mAh/g	~3.6 V	200-260Wh/kg	Improved variation of LiNiMnCoO ₂ by increasing amount of Ni and replacing Mn with small amount of Al

For anodes, the overwhelming majority of LIBs utilize graphite as the anode material. To improve the overall capacity of LIBs, the current electrode materials must be replaced by

new materials with higher Li storage capacity. In this thesis, focused on developing Si-based anode materials to replace the conventional graphite anodes. Among many candidates of high-capacity anode materials such as Ge (1623 mAh g^{-1}) and Sn (994 mAh g^{-1}),⁷⁻⁸ Si is considered as the most promising one due to its highest capacity of 4200 mAh g^{-1} , which can be attributed to high Li content in the fully lithiated Si with a composition of $\text{Li}_{22}\text{Si}_5$.⁹ As the comparison, the capacity of graphite is only 372 mAh g^{-1} based on the composition of fully lithiated graphite (LiC_6).¹⁰

1.1.1 Lithium-Ion Battery Working Mechanism

A typical Li-ion battery is made up of a negative electrode (anode) and positive electrode (cathode) soaked in electrolyte and separated by a separator, is shown in **Figure 1.1**.

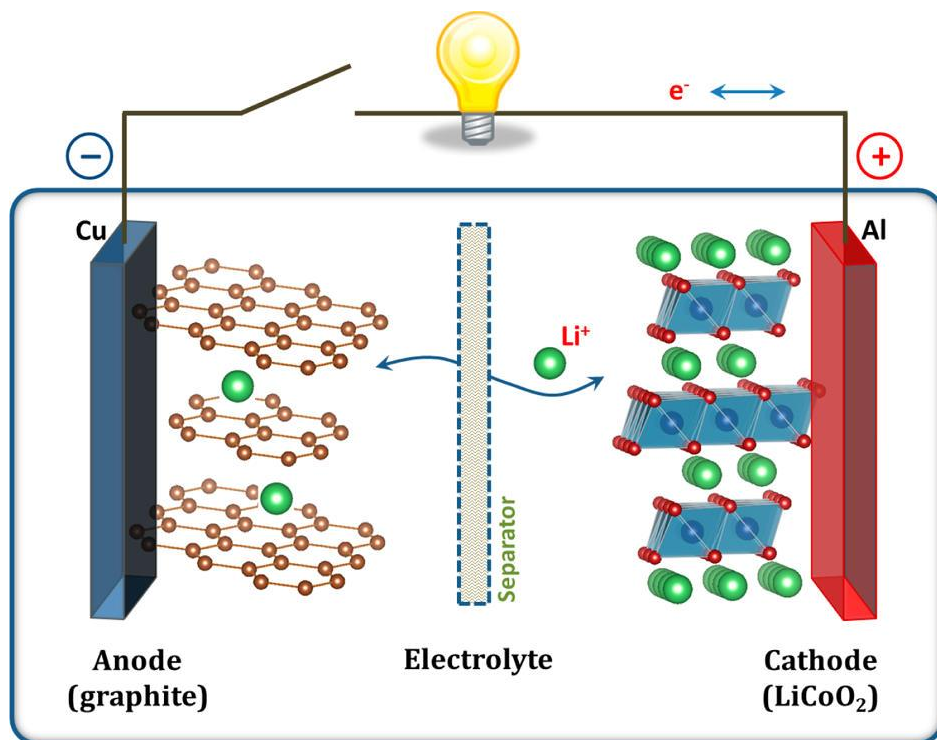
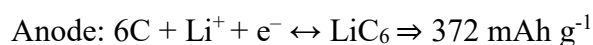


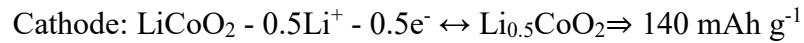
Figure 1.1 Schematic presentation of Li-ion battery.¹¹ Reprinted with permission from ref.

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The working mechanism is chemical reaction between anode and cathode. When discharging the battery, an oxidization occurs at the anode side and reduction occurs at cathode side. Electrons traverse external circuit and be consumed. Li ions extract form the anode, transport and insert into the cathode via conductive medium. When charging, Li ions go to reverse way. In this case, it is a wildly commercialized battery type.

Graphite as anode and lithium cobalt oxide as cathode. The reaction can be presented as:





1.1.2 Battery Performance and Improvement

There are many technical terms describing and using in battery field. Commonly seen is voltage (V), capacity (Ah), energy density (Wh/kg or Wh/l), C-rates. Energy Density is one of most important parameters. The specific capacity can be calculated via following formula:

$$\text{Energy Density} = \frac{\text{Specific Capacity of Electrode} \times \text{Electrode Weight}}{\text{Battery Weight (Volume)}} \times \text{Voltage}$$

Figure 1.2 show the specifications of state-of-the-art of current battery technology. The right lists all the components and parameters of current technology Panasonic NCR18650B cylindrical cell. Energy density calculation is based on the equation of capacity of electrode times electrode weight, divided by total weight times the nominal voltage. To be specific, the electrode capacity is the graphite capacity 300mAh/g multiplies the weight ration 0.95 which is 285mAh/g. Then multiplying anode weight 11.4g. Divided by total weight of battery 48.2g time the nominal voltage 3.6V. Finally, then energy density of Panasonic cell is 243wh/kg.

Weight (g)	NCR18650B
Packaging foil	0.31
Steel can	3.65
Insulator discs	0.13
Positive pole components	1.56
Negative pole	0.69
Cu CC	3
Anode mass	11.4
Al CC	2.6
Cathode mass	17.4
Separators	1.5
Ni mandrels	0.56
Electrolyte	5.4
Total weight	48.2
Inactive mass, sans electrolyte	15.1
Cathode	
area (cm ²)	372.1
active weight fraction	0.9
active material capacity (mAh/g)	200
Nominal Voltage (V)	3.7
Anode	
area (cm ²)	334.3
active weight fraction	0.95
active material capacity (mAh/g)	300
Nominal Voltage (V)	0.1

Figure 1.2 specifications of state-of-the-art of current battery technology.¹² Reprinted with permission from ref. 12. Copyright 2015 John Wiley and Sons.

In order to improve the batteries performance, next generation anode material silicon was introduced. A prediction was conducted. assumed the parameters keep the same except the anode material capacity become variable. anode mass, matching cathode mass become dependent variable. And nominal voltage slightly different 3.4V. The **Figure 1.3** is prediction. The green line is graphite-based cell energy. If the electrode specific capacity goes up to 500mAh/g, the areal loading can be reduced by more than half, if jump to 800mAh/g, the areal loading only needs less than a quarter of graphite loading amount.

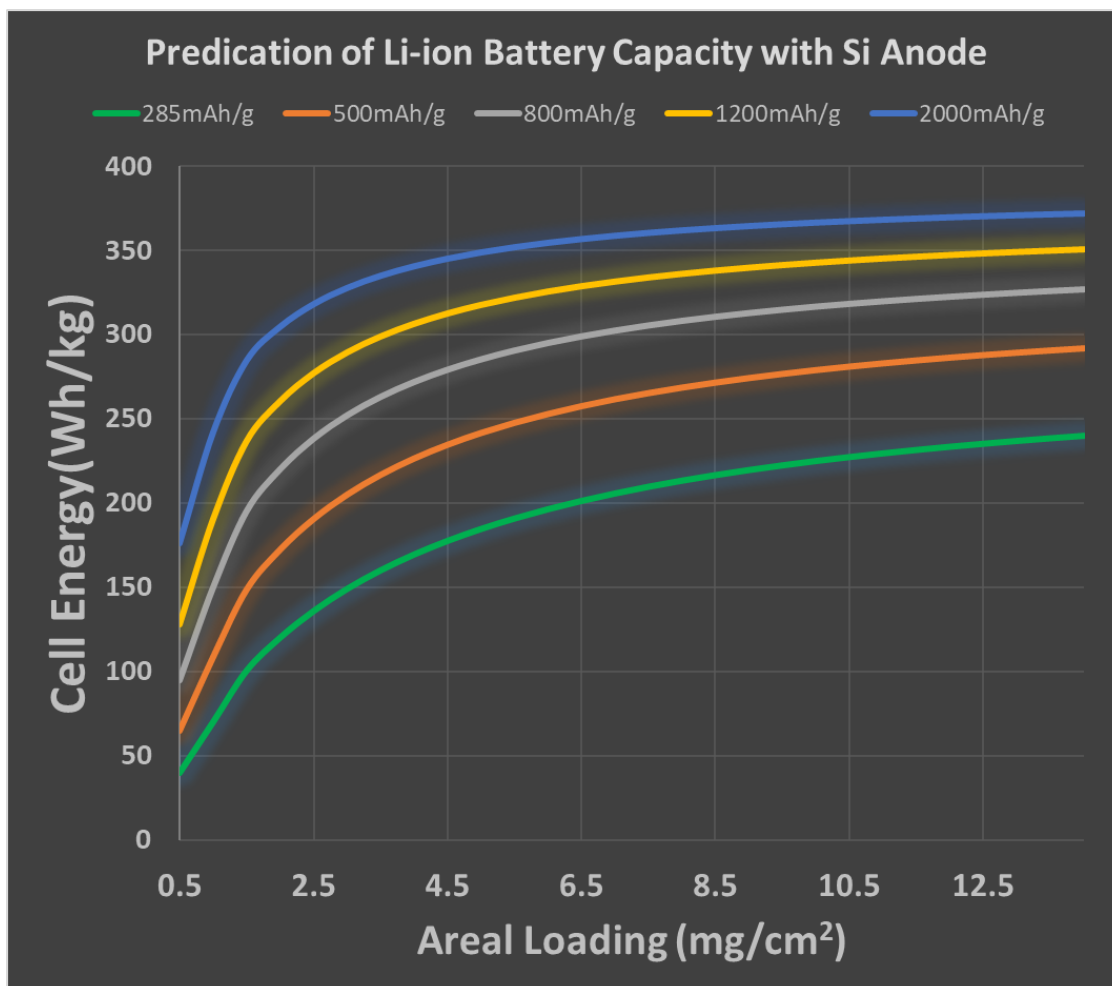


Figure 1.3 prediction of Li-ion battery using Si anode.

1.2 Silicon as Advanced Anode Material for Lithium-ion Batteries

Graphite has dominated the lithium-ion (Li-ion) batteries market as anode materials for decades. It has theoretical specific capacity as high as 372 mAh g^{-1} . With blooming electric vetches and portal customer portable electronic devices market. Nowadays, current battery technologies struggled to meet the increasingly demanding. The Silicon (Si) as a candidate

of anode material has been considered the most promising for next generation lithium-ion batteries, due to its ultra-high theoretical capacity of 4200mAh g^{-1} , which is 10 times higher than most widely commercialized anode material graphite. However, technical challenges including electrode fracture and particles pulverization induced by up to 300% of volume change during the transition between lithiation and delithiation, the formation of unstable solid-electrolyte interphase (SEI) and intrinsic poor conductivity of Si has hindered the practical applications of Si-based anode materials. Particles pulverization can be prevented by nanosizing Si particle beneath the critical breaking size, which no longer be regarded as a primary challenge. The constantly volume change could destabilize the SEI, continual electrolyte decomposition and accompanied with the poor conductivity of Si, resulting in irreversible capacity loss, eventually result in cell failure. Nowadays, particle applications of Si/graphite composite as hybrid anode is unable to address the issues caused by Si volume change. A widely used promising method is Si-C composite, conformal coated carbon as secondary structure is used to accommodate Si volume change during lithiation and delithiation and provide better conductivity. Various nanostructures of Si-C composites have been reported, such as sandwich-structured Si nanoparticles, pomegranate-like Si-C, yolk-shell Si-C and carbon coated Si. However, the primary nanosized silicon usually been synthesized via liquid chemical method or chemical vapor deposition using silicon (IV) chloride (SiCl_4) or pyrophoric silane (SiH_4), which is costly,

non-environmentally friendly and unscalable, limiting the commercial application. Magnesiothermic reduction reaction (MRR) has gained attention since Bao and co-workers reported that SiO₂ can be reduced by Mg and regraded as a promising synthesis method for Si. It is inexpensive, high scalable. Many studies had been conducted and reported that Si materials reduced by Mg exhibited good electrochemical performance. However, there remains some challenges, one is hard to preserve original SiO₂ structure during this violently exothermic reaction, since high local temperature could surpass the Si melt point. Luo and coworkers reported using NaCl to absorb larger amount heat generated by MRR preventing Si nanoparticles aggregation and structural failure. Another challenge is byproducts formation during magnesiothermic reduction, despite the product of Si and magnesium oxide (MgO), such as magnesium silicate (Mg₂SiO₄) or magnesium silicide (Mg₂Si). Therefore, in this work, we report utilizing magnesiothermic reduction of spray-dried SiO₂ derived from commercial SiO₂ to synthesize high-performance Si-C composite: $\text{SiO}_2 + 2\text{Mg} \rightarrow \text{Si} + 2\text{MgO}$. Uniform carbon coating via CVD not only form a buffer layer but also improve the conductivity of the composites and promote stable solid electrolyte interphase (SEI) layer formation on the Si surface, which is significant to the performance of Si anode material. Meanwhile nanosized Si particles and created void space through magnesiothermic reduction reaction can alleviate particle pulverization and accommodate volumetric expansion of Si induced by lithiation.

1.2.1 Mechanism of Silicon Lithiation

Currently, the commercial Li-ion batteries usually contain graphite as anode (negative electrode) and lithium metal oxide (LMO) or lithium iron phosphate (LiFePO_4) as cathode (positive electrode). Both conventional anode and cathode followed the mechanism of intercalation. The Li ions react with traditional anode and cathode materials via inserting or extracting in or out interstitial sites of host lattice. This type of reaction mechanism, small strains result in minimal volume change which can provide good reversibility, cycle stability and capacity retention, although limited storage space can limit the capacity. The electrochemical reaction mechanism of Si upon lithiation is different from graphite. Instead of intercalation mechanism, Si follows a conversion type of reaction mechanism-alloying. This type of reaction mechanism involves bonds formation and breaking forming Li-Si alloying which can provide much higher capacity because of unconstrained storage space, however, forming stronger bonds than intercalation, the reversibility, cycle stability and capacity retention are impacted.¹³

At the beginning cycle of lithiation of Si follows two phase transformation mechanism.¹⁴ Because of the strong Si-Si bonds need to be weaken via huge activation energy, so at first, from many studies, found formation of amorphous Li_ySi ($0 < y < 3.4 \pm 0.2$). At amorphous phase formation process results in the large portion of volume expansion and cause most strains. Within the reaction processing, subsequently, Highly lithiated (lithium rich)

amorphous Li_ySi form. Many studies about Li-Si alloying crystalline phase changes has been conducted via *in situ* X-ray powder diffraction.¹⁵⁻¹⁶ Obrovac et al.¹⁵ found that suddenly transformation from amorphous lithated Si to crystalized $\text{Li}_{15}\text{Si}_4$ when lithiation potential went below around 60 mV vs Li/Li^+ .

The Li-Si phase diagram shows below. The full lithiation $\text{Li}_{22}\text{Si}_5$ phase could exist at temperature at high temperature, which renders as high as 4200 mAh g^{-1} theoretical specific capacity. The reaction can be described as: $5\text{Si} + 22\text{Li}^+ + 22\text{e}^- \leftrightarrow \text{Li}_{22}\text{Si}_5 \Rightarrow 4200 \text{ mAh g}^{-1}$. However, at near room temperature, full lithiation phase exists $\text{Li}_{15}\text{Si}_4$: $4\text{Si} + 15\text{Li}^+ + 15\text{e}^- \leftrightarrow \text{Li}_{15}\text{Si}_4 \Rightarrow 3580 \text{ mAh g}^{-1}$.

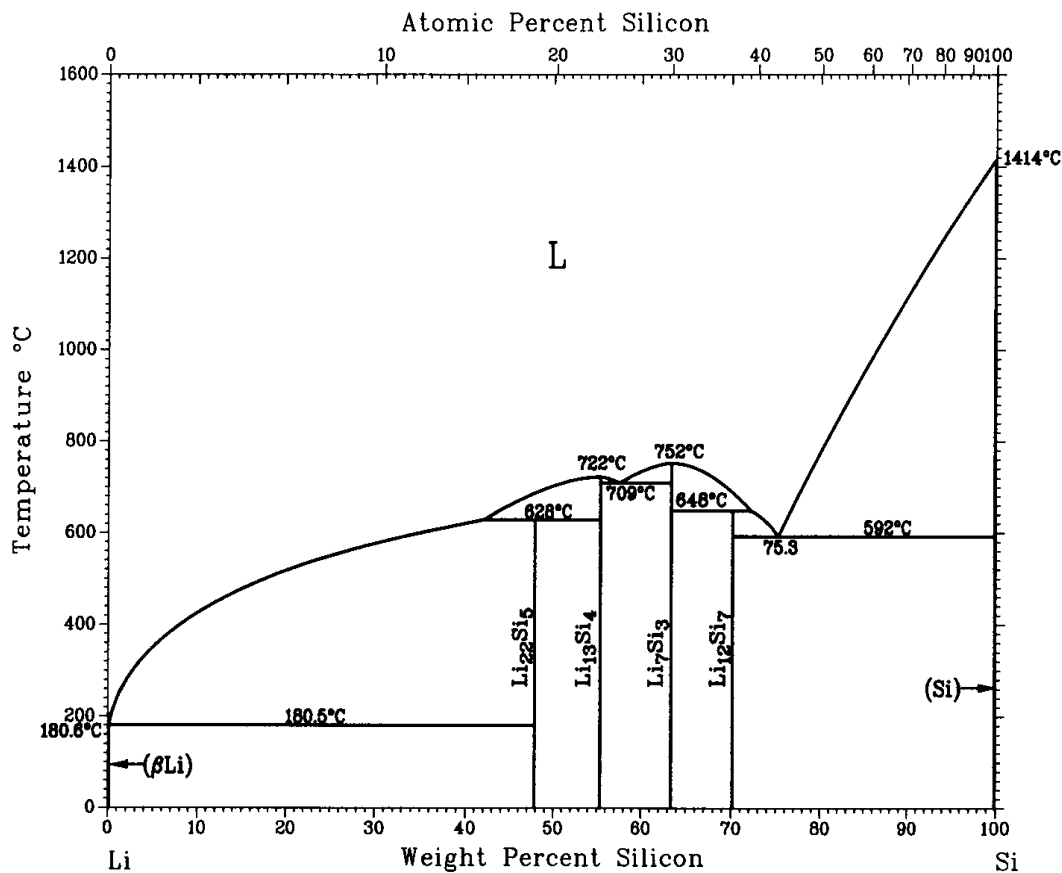


Figure 1.4 phase diagram of the lithium–silicon system.¹⁷ Reprinted with permission from ref. 17. Copyright 1990 Springer.

Figure 1.5 shows the typical silicon charge discharge curve. At the voltage between around 1.2 V and 0.12 V. The capacity mostly contributed by surface reaction formation of solid electrolyte interphase (SEI). The lithiation of silicon initiated around 0.12 V, then a plateau

was formed and lithiation ended at 0.01 V. Upon charge, Si delithiation and formed plateau at the voltage window at 0.2 V to 0.6 V.

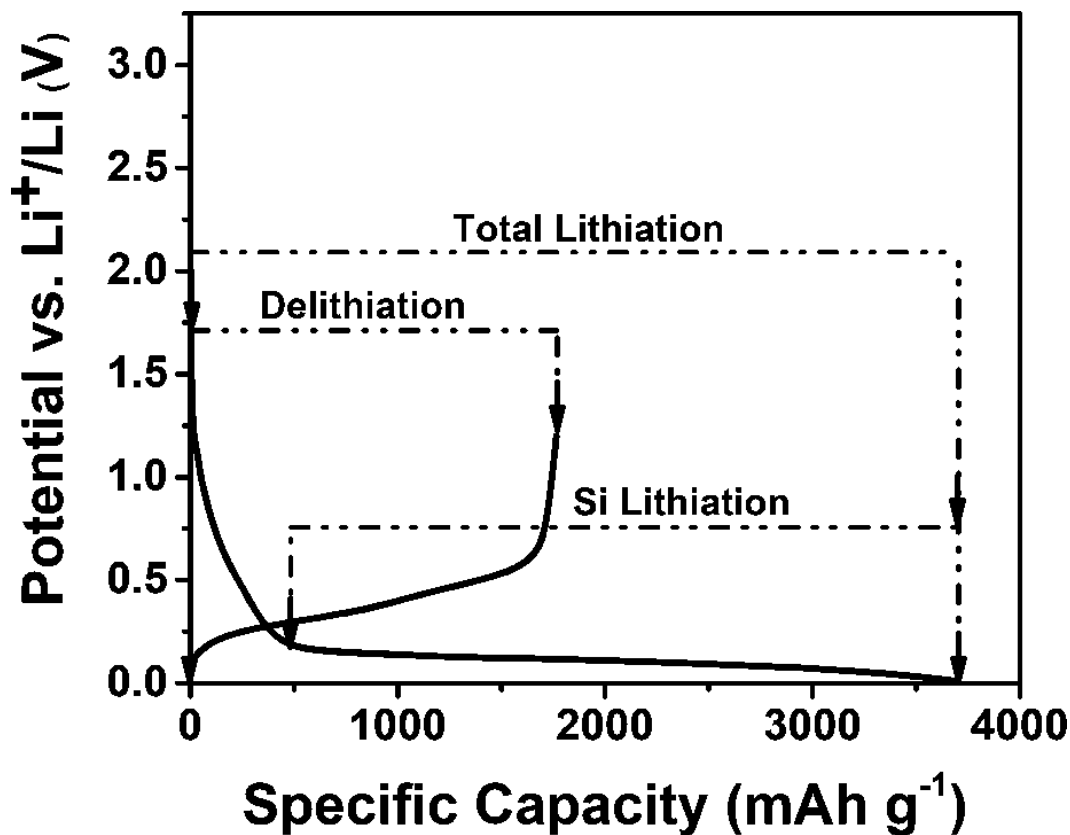


Figure 1.5 schematic lithiation and delithiation curve of silicon.

Typically, in Li-ion system, the electrochemical, upon lithiation, crystalline silicon reacted with lithium formed amorphous lithium-silicon alloys. Then Silicon nearly reach lithiation state, the amorphous Li-Si phase convert to crystalline $\text{Li}_{15}\text{Si}_4$. At the charge state, lithium rich silicon phase started delithiation. At early and middle stage, $\text{Li}_{15}\text{Si}_4$ partially converted

to amorphous Li-Si alloys and electrochemical characteristic is a large plateau between the voltage of 0.01 V and 0.6 V. Once the $\text{Li}_{15}\text{Si}_4$ transformed to Li_2Si or less Li lithiated Si, the $\text{Li}_{15}\text{Si}_4$ disappeared and Si become amorphous. In the following cycles, the phase transformations were between amorphous Li-Si to crystalline $\text{Li}_{15}\text{Si}_4$. Detail show in **Figure 1.6**.

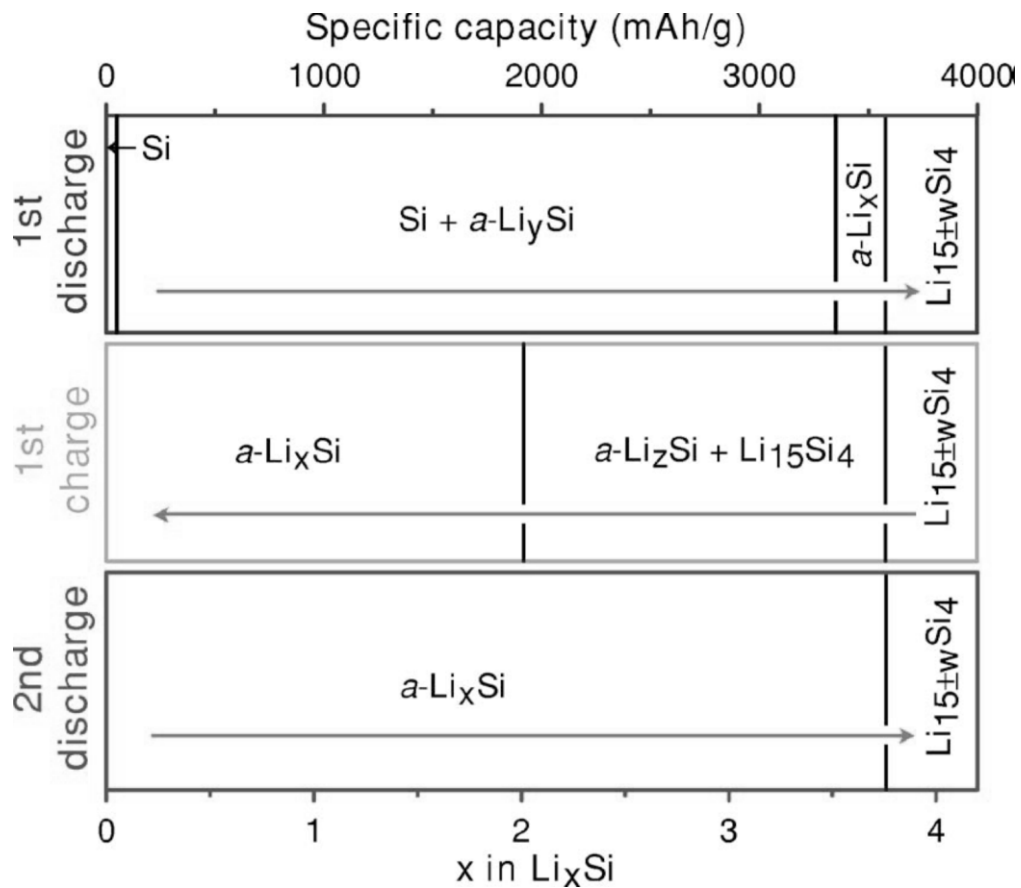


Figure 1.6 phase transformation within lithiation and delithiation.¹⁸ Reprinted with permission from ref. 18. Copyright 2007 Electrochemical Society

In summary, the Si electrochemical lithiation mechanism follows the two-phase reaction, forming amorphous lithated Si from crystalline Si. In addition, lithiation potential falls below 60 mV vs Li/Li⁺ crystalized Li₁₅Si₄ phase formation occurs.

1.2.2 Silicon Electrode Failure Mechanism

Despite that alloy type anode materials have the unparalleled higher gravimetric and volumetric capacities compared to intercalation types of anode (graphite), because more lithium atoms need to be restored in the host, Si has up to ~300% anisotropic volume expansion once been fully lithiated. The dramatic volume fluctuation during lithiation and delithiation introduce large strain and stress which result in Si particles cracking and pulverizing. One big challenge is the large volume change resulting in particle pulverization and electrodes cracking and fracture as shown in **Figure 1.7**.

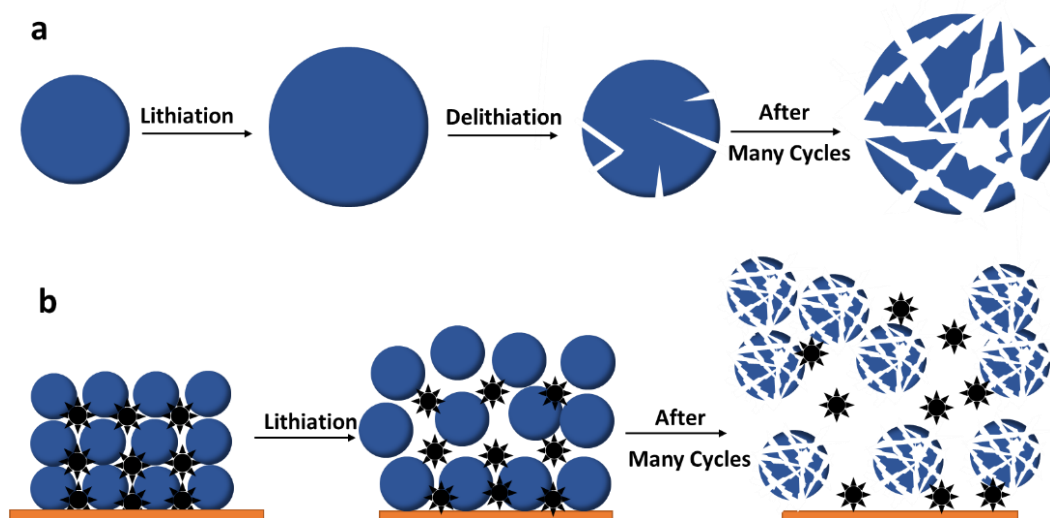


Figure 1.7 Failure mechanisms of Si electrode. a) Si particles cracking and pulverization; b) electrode cracking and delamination.

Because of particles pulverization resulting from volume expansion, can lead Si particles fall apart and separate from conductive agent, even some material unable to connect to current collector result in bad electric conductivity inefficient electrons transportation. Eventually some particles been isolated. From the electrode degradation aspect, volume change introduces expansion and shrink of particles weaken the binding of binder, which enable the delamination of materials which leading to the anode capacity fading. With proceeding the cycling, more materials breaking away and isolating from conductive environment results in bad cycle stabilities. This type of failure mechanism will eventually lead to dramatic capacity decay.

Another challenge is the unstable solid-electrolyte-interphase (SEI) formation on the Si surface. The failure mechanism is shown in **Figure 1.8**.

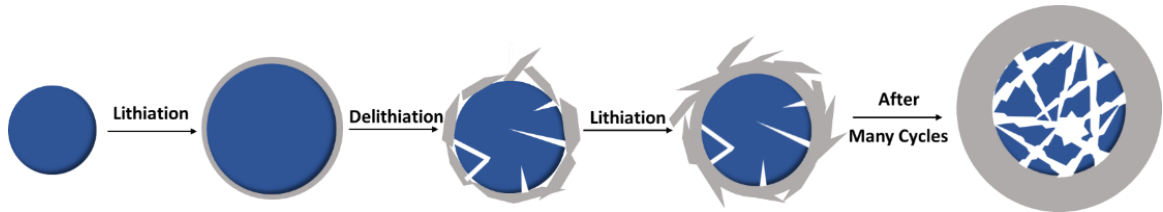


Figure 1.8 SEI formation on Si surface.

As part 1.1.1 mentioned, the lithiation potential of crystalline Si initiates is around 0.12 V (Li^+/Li), which is much lower than the reduction of potential (typically above 1.0 V Li^+/Li) of carbonates solvents such as ethylene carbonate (EC) and diethyl carbonate (DEC) which were commonly used as Li salts solvents.¹⁹ Therefore, the SEI layer is inevitable during lithiation step. Unlike intercalation type of anode-graphite, because of continuously volume change, the passivating layer reduced from electrolyte on the Si surface would never be stabilized, just as **Figure 1.8** shows. After lithiation, the fully lithiated Si forms a layer of SEI. Subsequently, after delithiation accompanying with volume shrink, the stresses are not only effective on Si particles but also on the SEI layer, the SEI breaks up. The follow lithiation cycle, the exposed Si surface will once again form new SEI layer with electrolyte. After many cycles, a thick SEI layer eventually grow on the Si surface. To be

noted that, SEI has the lithium-ion conductivity but electron transportation ability.²⁰ Therefore, forming thick SEI eventually results in Si isolated from electric environment. Unstable SEI has huge impact on the Si anode performance. Meanwhile, continuously SEI breaking and reforming consuming large amount of electrolyte and Li resource which is unacceptable in commercial battery system which injecting lean electrolyte.

1.3 State of Art of Silicon Anode Materials

To solve the disadvantages of cracking and pulverization and unstable SEI of Si. Many studies have been conducted to overcome those challenges.²¹⁻³³ To address the mechanical degradation of bulk Si particle, reducing Si size became a good solution. Recently, Huang et al.³⁴ Si particle size smaller than 150 nm can effectively avoid fracture. Cui et al.³⁵ found the critical fracture size of Si nanopillars were around 240-360 nm, for the Si nanowires were 300-400 nm. In conclusion, as long as engineering Si particle lower than critical fracture size, can efficiently accommodate the strain and stress introduced via lithiation. For example, Fultz et al.³⁶ reported nanostructured Si particles and films demonstrates good performance over bulk Si.

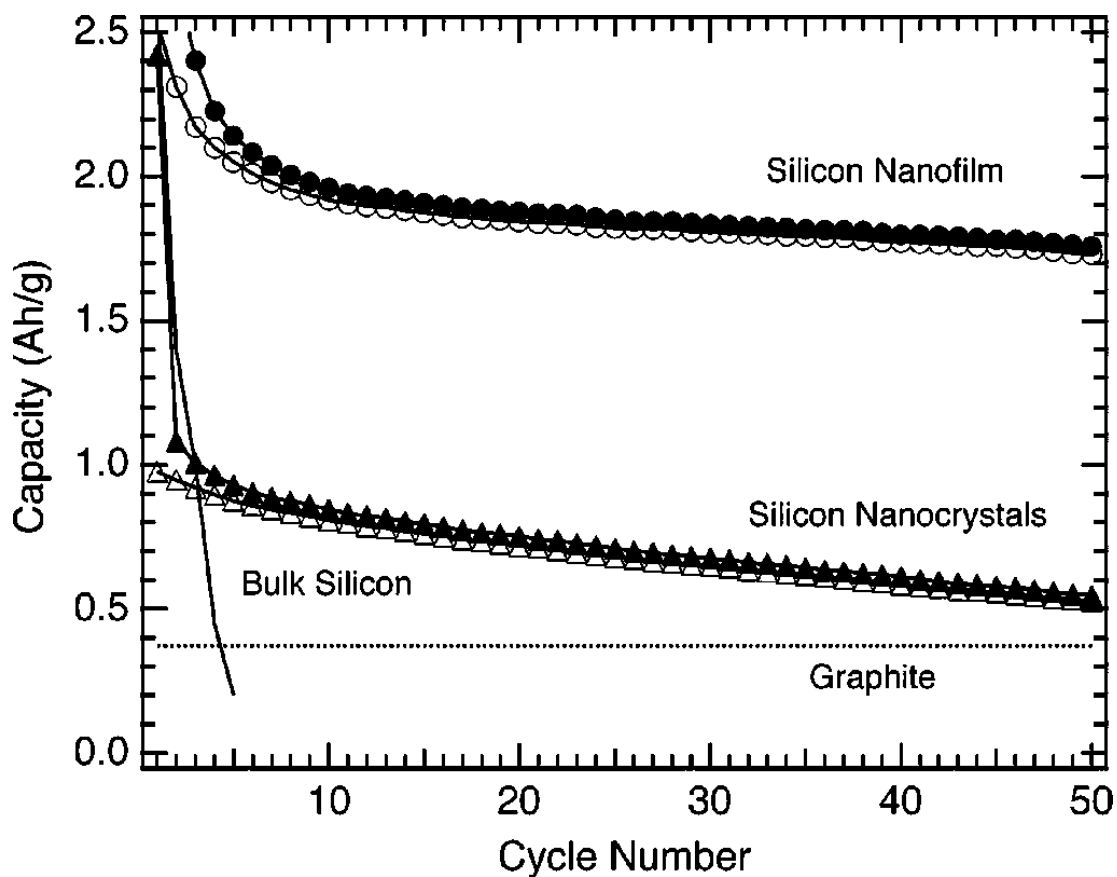


Figure 1.9 cycle stabilities of nanostructured Si and bulk Si.³⁶ Reprinted with permission from ref. 36. Copyright 2007 Electrochemical Society

Cui et al.³² reported a high-performance Si nanowires (Si NWs) with high reversible capacity close to theoretical and good cycle stability. As shown in **Figure 1.10**, crack and fracture preventing Si NWs were synthesized via catalytical vapor-liquid-solid (VLS) growing on stainless steel substrates.

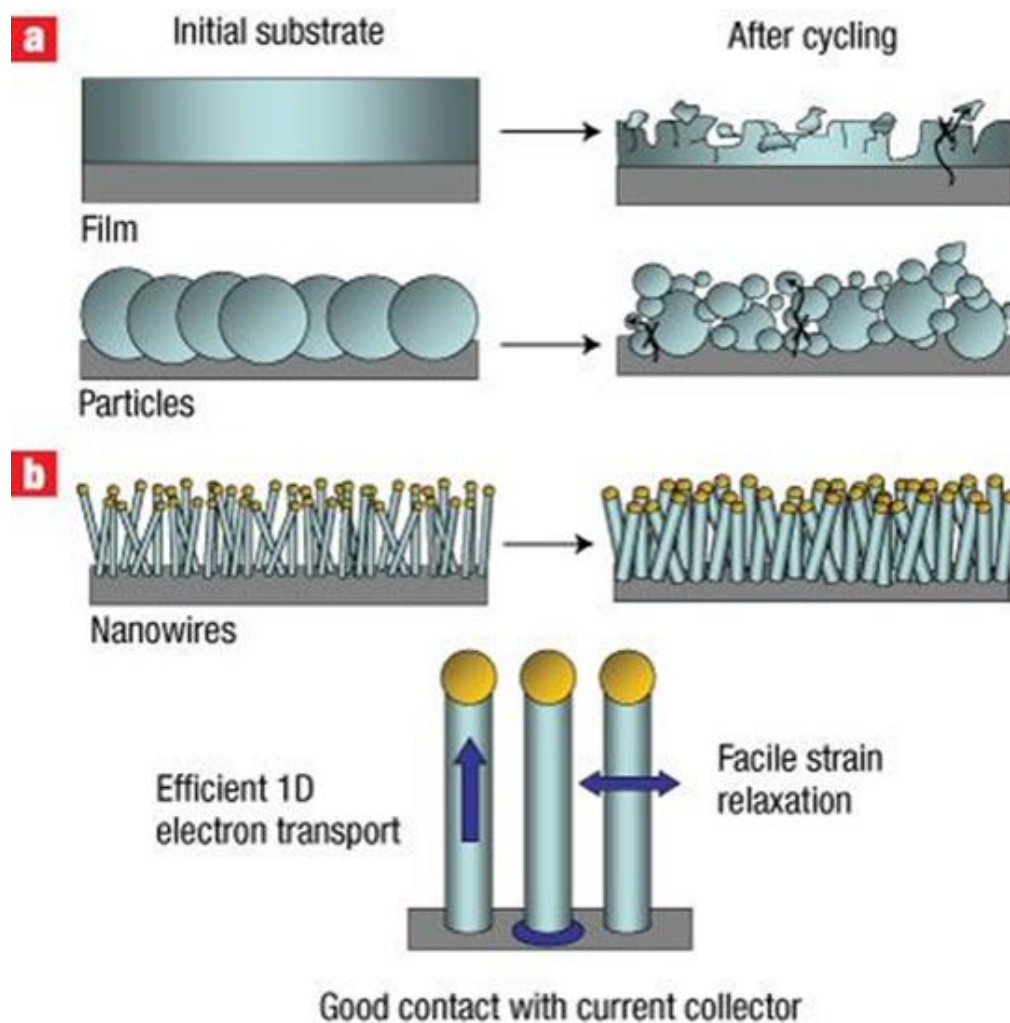


Figure 1.10 schematic of morphological changes that occur in Si during electrochemical cycling.³² Reprinted with permission from ref. 32. Copyright 2007 Springer Nature

Another method effectively improve Si anode performance is by forming composite with conductive materials to improve structural stability and conductivity. Yushin et al.³⁷ reported a Si coated carbon black composite using annealed carbon black as backbone via

Si chemical vapor deposition and carbon chemical vapor deposition. The synthesis routine is shown in **Figure 1.11**.

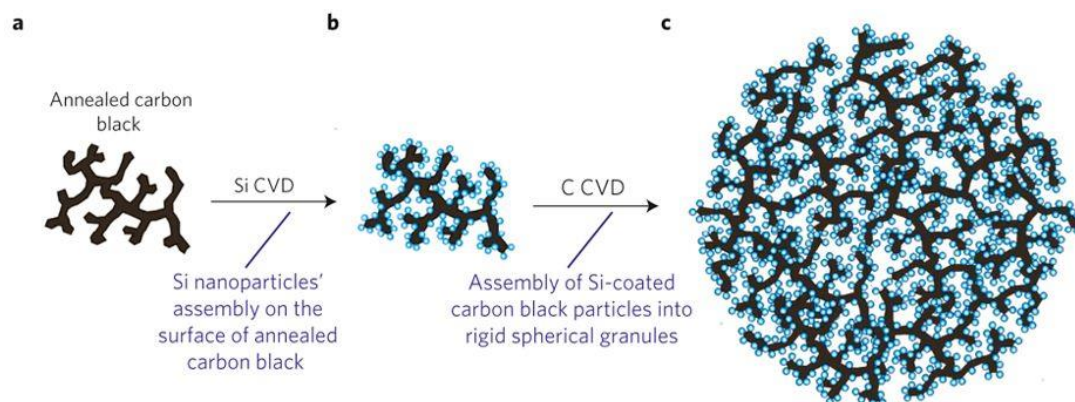


Figure 1.11 schematic of synthesis of Si coated carbon black composite (a)-(b) carbon black Si coating via Si CVD; (b)-(c) carbon CVD coating and rigid spherical composite assembling.³⁷ Reprinted with permission from ref. 37. Copyright 2010 Springer Nature

This Si-C composite shows a noticeable excellent performance of capacity of 1950 mAh g⁻¹, which is ~ 6 times as current graphite anode. In addition, the Si carbon black composite extends a good rate capability and excellent cycle stability. The performance as shown in **Figure 1.12**.

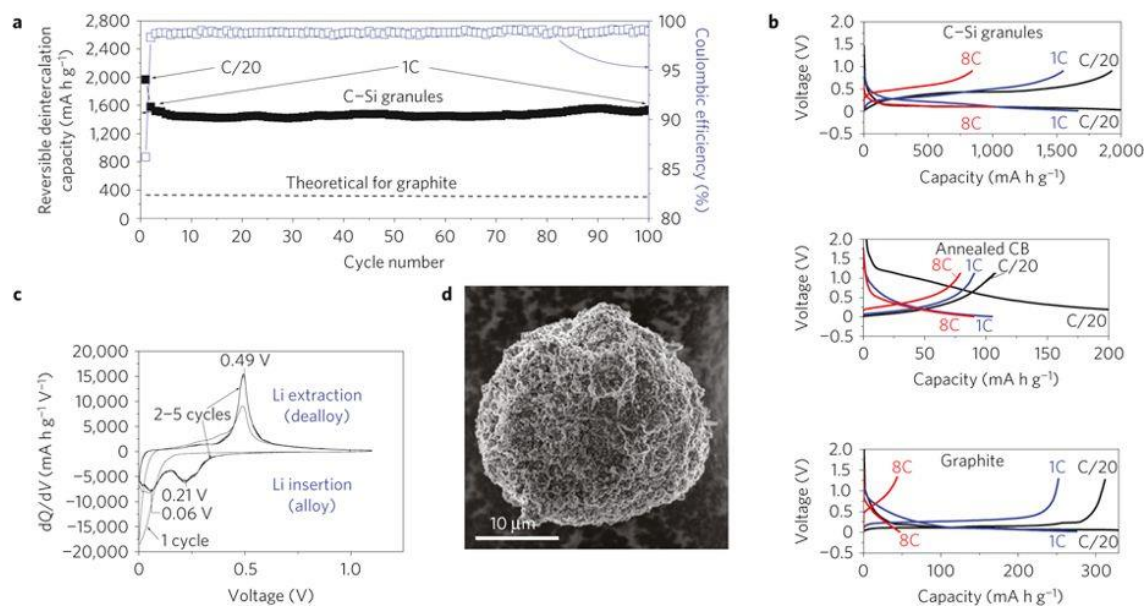


Figure 1.12 (a) delithiation capacity of Si-C composite compared with graphite theoretical capacity as reference; (b) representative lithiation and delithiation curves of Si-C composite anode at rates of $\sim$ C/20, 1C and 8C compared with carbon black and commercial graphite anode within working window at 0 - 1.1 V; (c) CV curves of the Si-C anode in the potential window of 0–1.1 V at scan rate of 0.025 mV s^{-1} .³⁷ Reprinted with permission from ref. 37.

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Kim et al.³⁸ reported another effective way, they utilized N-doped carbon nanotube (CNT) and graphene mixed with commercial Si particles self-assembling at room temperature. By the doping method, the Si-C anode materials reveals a remarkable cycle stability and rate performance. The synthesis method shows in **Figure 1.13**.

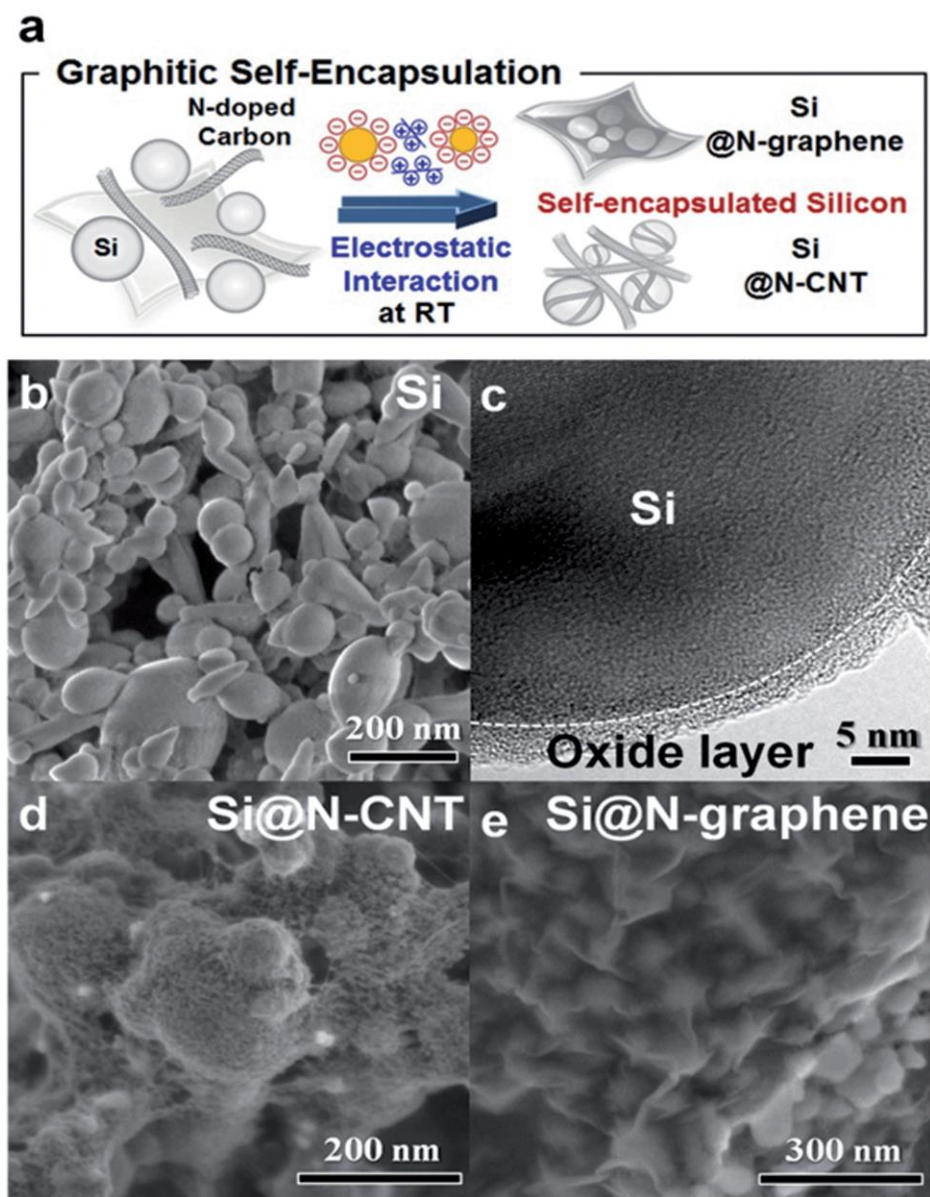


Figure 1.13 (a) a schematic shows graphitic carbon and Si self-assembling routine; (b) HR-SEM of commercial Si particles (c) HR-TEM images of Si particles and passivating oxidation layer was observed; (d) HR-SEM images of Si and N-CNT composite (e) HR-SEM images of Si and N-graphene composite.³⁸ Reprinted with permission from ref. 38.

Controlling morphologies of Si also been regarded as one of feasible methods. Such as Si thin films and their composites, which can moderately accommodate the volume change induced by lithiation and delithiation and relief the mechanical degradation.³⁹⁻⁴³ Si thin films usually attached on a conductive substrate and employed as anode without binder and conductive agent. Generally, Si thin films are produced via chemical vapor deposition (CVD) or physical vapor deposition (PVD). Jiang et al.⁴¹ reported Si thin films which can effectively relief stress. Different approach reported by Cui et al.⁴² using plasma-enhanced chemical vapor deposition (PECVD) coating a thin layer on CNT and nanocellulose fibers (NFC) then coating on regular paper. They demonstrated an excellent cycle life with stable capacity of 1200 mAh g⁻¹. The morphology shows in **Figure 1.14**.

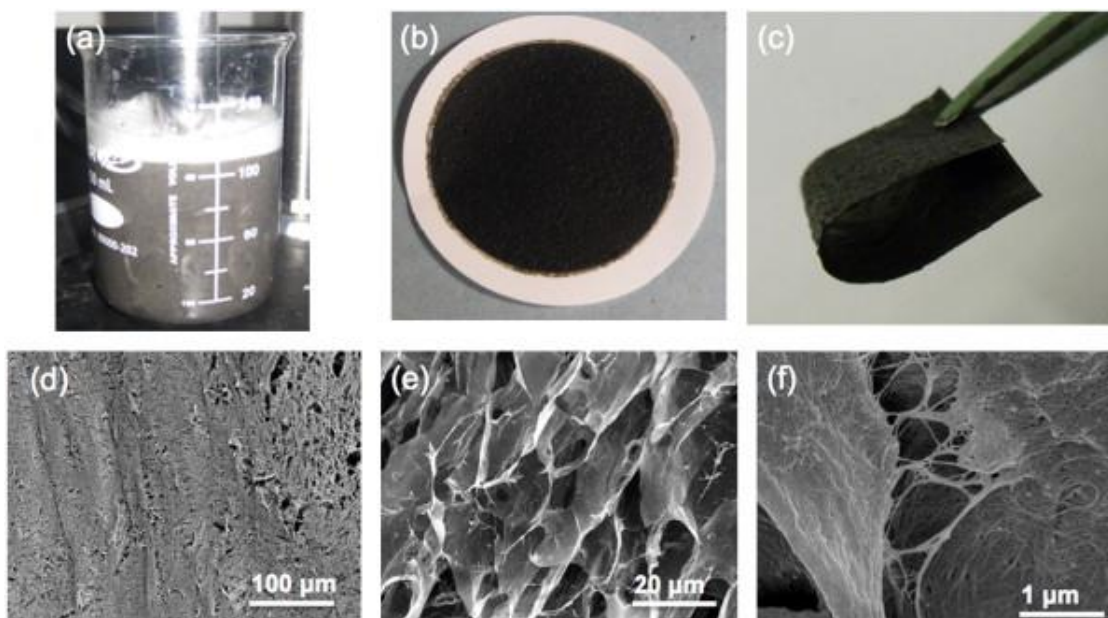


Figure 1.14 fabrication process of Si CNT & NFC nanopaper. (a) CNTs aqueous dispersion of and nanocellulose fibers; (b) a film made of CNT and NFC slurry which dewater from (a); (c) Si CNT & NFC nanopaper via freeze drying; (d)–(f) SEM images of morphologies of nanopaper.⁴² Reprinted with permission from ref. 42. Copyright 2012 Elsevier Ltd.

Thin films can moderately address the Si particle pulverization and manage mechanical degradation, however, the issue induced by unstable SEI still remained. These reports show that thin Si films electrode will show electrode degradation or even failure after hundreds cycle.⁴⁴ the electrodes cracking images shows in **Figure 1.15**.

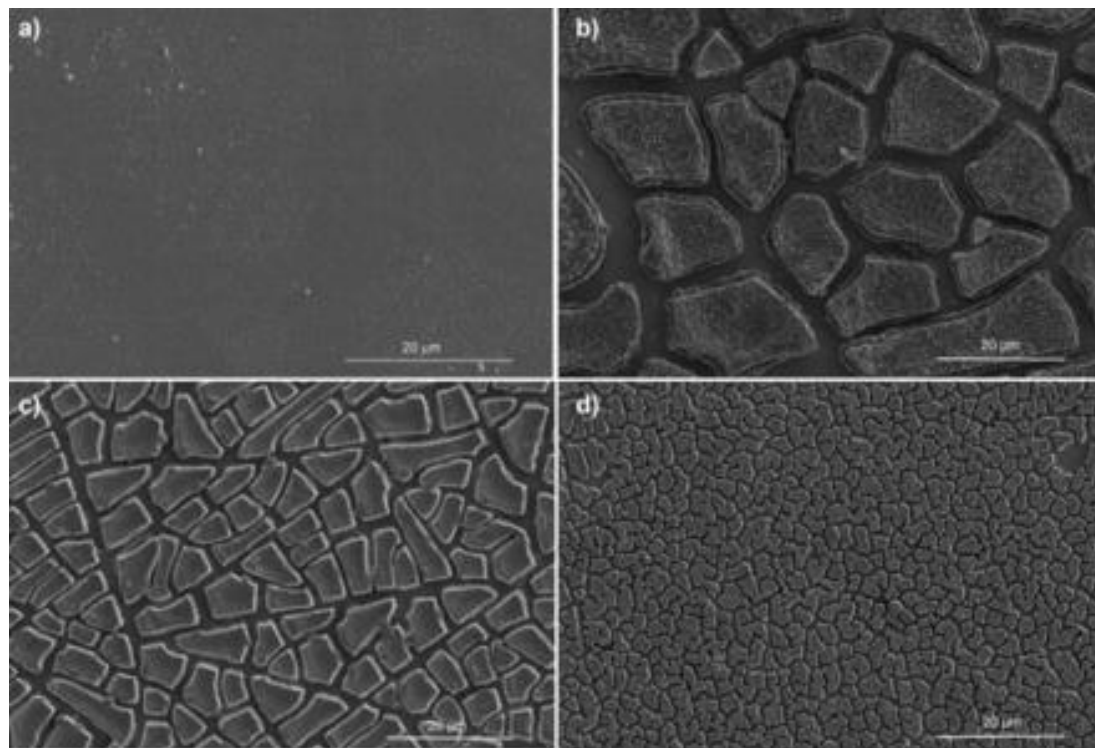


Figure 1.15 (a) SEM image of a pristine 500 nm thickness of Si film (b) 1000 nm thickness of Si film after 5 cycles. (c) 500 nm thickness of Si film after 5 cycles. (d) 200 nm thickness of Si film after 10 cycles.⁴⁴ Reprinted with permission from ref. 44. Copyright 2014 Electrochemical Society

A more effective structure design was developed. This method coating and encapsulating a stable layer on Si nanoparticles to address the unstable SEI. The benefit of the stable layer offers not only a protection of the continues decomposition of electrolyte but also a conductive agent to make up the instinct poor conductivity of Si. In addition, engineering

an empty space to accommodate volume change. Cui et al.³³ reported a pomegranate-like Si@void@C yolk shell structure composite. The synthesis routine shows in **Figure 1.16**.

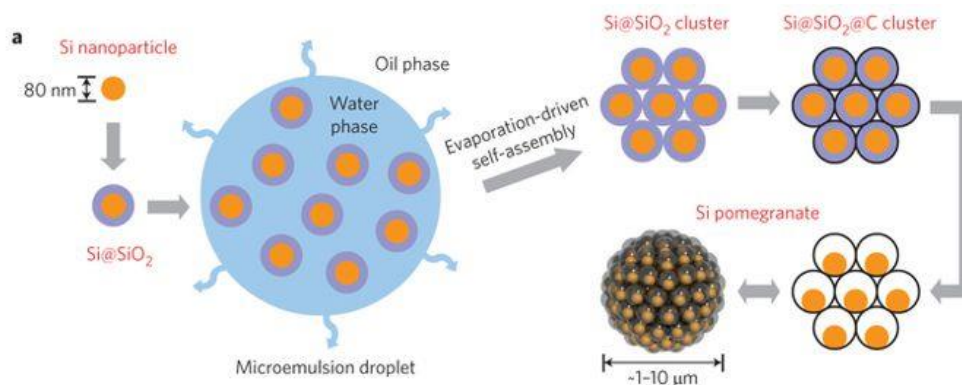


Figure 1.16 synthesis routine of Si@void@C composite.³³ Reprinted with permission from ref. 33. Copyright 2014 Springer Nature

Commercial Si nanoparticle was firstly encapsulated by a silica layer. Then via microemulsion and evaporation, Si@SiO₂ cluster was collected and encapsulated by resorcinol-formaldehyde resin followed by carbonization and subsequently washed with HF acid. The final product Si@void@C composite was obtained. This Si based anode material shows an excellent cycle stability with capacity retention of 97% (1000 cycles vs initial cycle). And realized over 1000 mAh g⁻¹ specific capacity during entire cycles. Thick electrode can achieve over 3 mAh cm⁻² with 3.12 mg cm⁻² areal loading after 100 cycles.

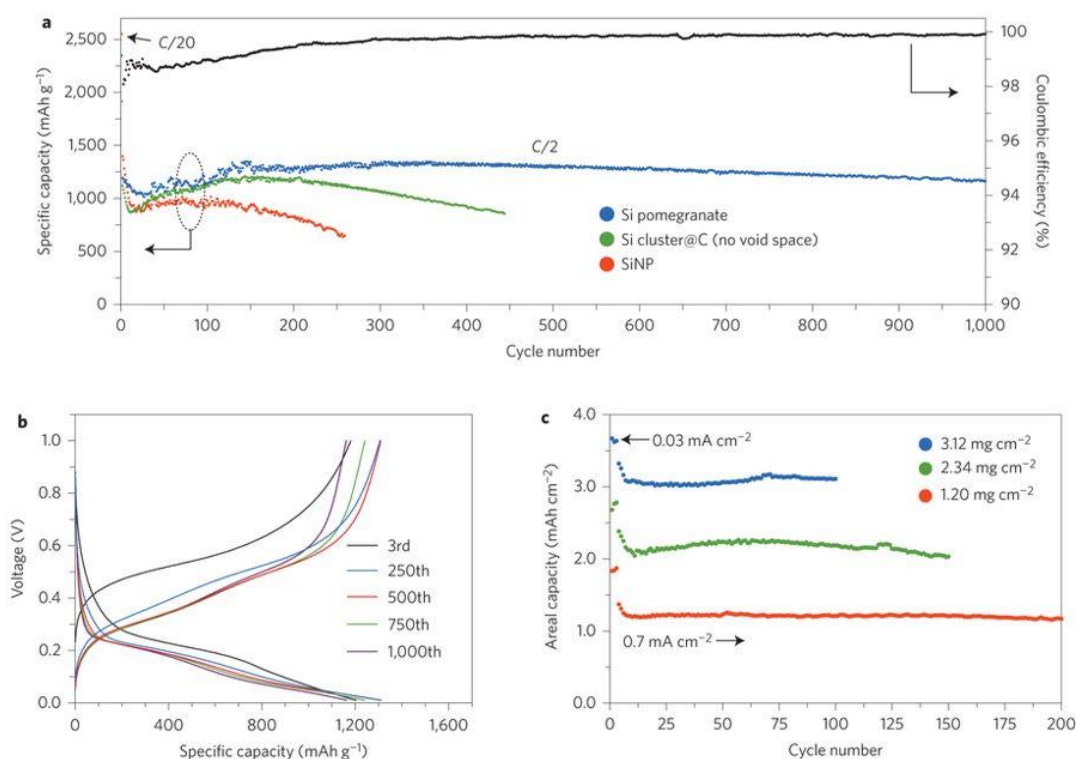


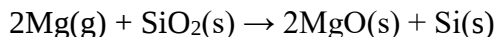
Figure 1.17 (a) delithiation cycle stability of 1,000 cycles of Si@void@C, Si@C and Si with Coulombic efficiency of Si@void@C. (areal loading: $\sim 0.2 \text{ mg cm}^{-2}$); (b) representative lithiation and delithiation curves of 3rd, 250th, 500th, 750th and 1,000th cycles; (c) cycle stability of high areal loading.³³ Reprinted with permission from ref. 33.

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The earliest investigation of porous silicon can be traced back to 1956.⁴⁵ Stain etching and anodic etching were used to make porous Si.⁴⁶⁻⁴⁷ However, Si particle size and pore size

unable to be effectively controlled make these technologies hard to practically realized in commercial LIBs.

The aforementioned methods all used commercial Si nanoparticles, Si nanowires, Si nanopillar, Si thin films or Si wafers silicon usually been synthesized via liquid chemical method or chemical vapor deposition using silicon tetrachloride (SiCl_4), trichlorosilane (SiHCl_3), silane (SiH_4) or disilane (Si_2H_6), which is costly, extremely flammable, non-environmentally friendly and unscalable, limiting the commercial application.^{22, 48-50} Bao et al.⁵¹ reported that silica can be reduced by gaseous magnesium:



Magnesiothermic reduction reaction (MRR) has gained extensive attention and been regarded as a promising synthesis method for Si. It is inexpensive, high scalable. Since that, many studies had been conducted and reported that Si materials reduced by Mg applied on the LIBs exhibited good electrochemical performance.^{1, 30, 52-60} Zhao et al.¹ reported a high-performance ordered mesoporous Si/C composite. Mesoporous SiO_2/C used as a precursor via magnesiothermic reduction converted to mesoporous Si/C. As shown in **Figure 1.18**.

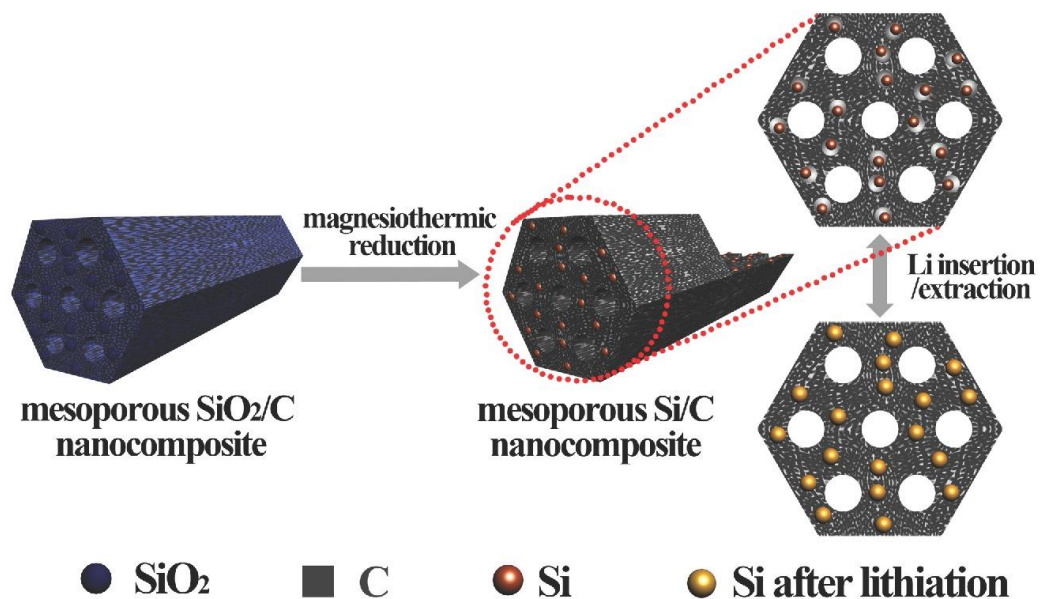


Figure 1.18 synthesis routine of mesoporous Si/C composite via MRR.¹ Reprinted with permission from ref. 1. Copyright 2014 John Wiley and Sons

The mesoporous Si/C composite extends an excellent capacity and cycle stability. The composite with realized $\sim 1800 \text{ mAh g}^{-1}$ at current rate of 0.5 A g^{-1} and excellent coulombic efficiency. In addition, at high current density of 2 A g^{-1} , capacity still can achieve $\sim 1500 \text{ mAh g}^{-1}$ and maintain it after 1000 cycles.

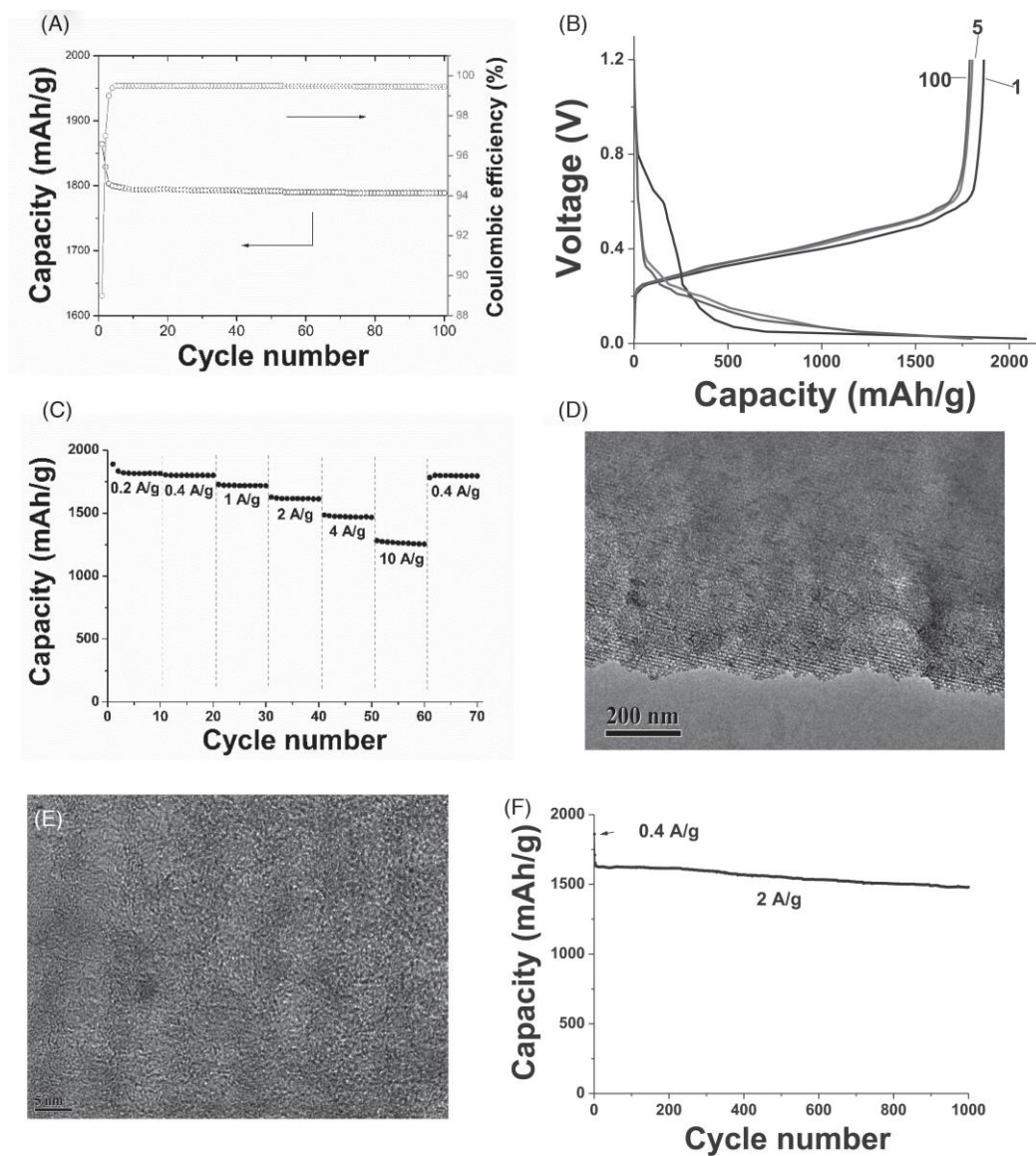


Figure 1.19 (a) cycle stability of mesoporous Si/C at current density of 0.5 A g^{-1} ; (b) representative lithiation and delithiation curves at 1st, 5th and 100th cycle; (c) rate capabilities at various current rate; (d) (E) TEM and HRTEM of Si/C after 100 cycles; (F) cycle stability of mesoporous Si/C at high current density of 2 A g^{-1} for 1000 cycles.¹

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1.4 Magnesiothermic Reduction reaction of Silica

Magnesiothermic reduction reaction has drawn attentions for years. However, there remains some challenges, one is hard to preserve original SiO_2 structure during this violently exothermic reaction, since high local temperature could surpass the Si melt point.⁶¹ Luo et al. reported using NaCl to absorb larger amount heat generated by MRR preventing Si nanoparticles aggregation and structural failure.⁶² Another challenge is byproducts formation during magnesiothermic reduction, despite the product of Si and magnesium oxide (MgO), such magnesium silicate (MgSiO_3 , Mg_2SiO_4), or magnesium silicide (Mg_2Si).^{53, 63} The products of MRR can be described by using Mg-Si-O ternary system phase diagram.⁶⁴ The side reactions can be predicted as well.

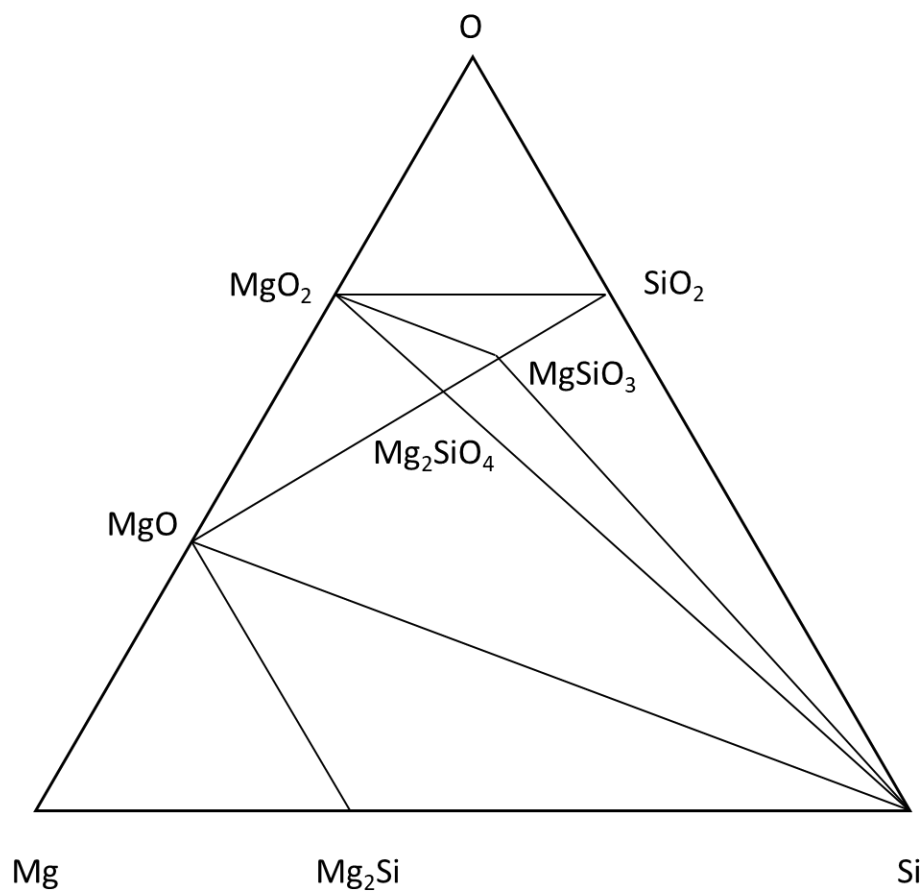


Figure 1.20 Mg-Si-O phase diagram at 298 K and 1 atm.⁶⁴ Reprinted with permission from ref. 64. Copyright 1992 American Chemical Society.

This reaction can be described as Mg reduces SiO_2 partially and forming magnesium silicate and Si: $2\text{Mg}(\text{g}) + 3\text{SiO}_2(\text{s}) \rightarrow 2\text{MgSiO}_3(\text{s}) + \text{Si}(\text{s})$. Then the silicate was further reduced by Mg forming Mg_2SiO_4 and partially reduced Si: $2\text{Mg}(\text{g}) + 4\text{MgSiO}_3(\text{s}) \rightarrow 3\text{Mg}_2\text{SiO}_4(\text{s}) + \text{Si}(\text{s})$. Subsequently, reduction of Mg_2SiO_4 occurred: $2\text{Mg}(\text{g}) + \text{Mg}_2\text{SiO}_4(\text{s})$

→ 4MgO(s) + Si(s). However, this is not the end of MRR. Excessive Mg will further reduce

Si to Mg₂Si: 2Mg(g) + Si(s) → Mg₂Si(s).

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Chapter 2. Silicon-carbon Anode Materials via Spray Drying and Magnesiothermic Reduction

2.1 Abstract

In this chapter reports a high-performance silicon-carbon (Si-C) composite anode material for lithium-ion (Li-ion) batteries via a scalable production route. Porous silica particles as the precursor of Si is obtained from aerosol spray drying of the commercial silica suspension in water. The silica particles are reduced to porous Si via magnesiothermic reduction followed by carbon coating from chemical vapor deposition (CVD). The kinetics of magnesiothermic reduction of silica is systematically studied thus the conversion and the microstructural properties of obtained porous Si can be precisely controlled to be optimal. The Si-C composite demonstrates excellent specific capacity of 1835 mAh g^{-1} and outstanding cycle stability. When used as an additive to the graphite anode, the thick electrodes with total areal loading of 4.0 mg cm^{-2} containing 20 wt.% Si-C and 70 wt.% graphite achieve remarkable performance: 850 mAh g^{-1} overall specific capacity and 3.4 mAh cm^{-2} areal capacity as well as 92% capacity retention after 200 cycles. Full cells composed of commercial lithium iron phosphate cathode and the Si-C-graphite anode under lean electrolyte condition also demonstrate excellent performance.

2.2 Introduction

Silicon (Si) is a high-capacity anode material that can replace or complement the graphite anode in the next generation lithium-ion (Li-ion) batteries.¹⁻¹⁴ Tremendous efforts from both academic and industrial sectors are devoted to commercialize Si-based anode materials in the near future.^{10, 15-18} However, successful cases of Si-anode commercialization are still scarce. The technical challenges are mostly originated from two fundamental properties of Si as a Li storage material: inevitable volume change during lithiation-delithiation and inferior electronic conductivity comparing to graphite. The former results to continuous degradation of the electronic connection in the electrodes and continuous rapture of the solid electrolyte interphase (SEI);^{3, 19-24} the latter seriously limits the areal loading of the Si-based materials in the electrode thus difficult to achieve practical high-capacity.^{9, 12, 25-27} In addition to addressing the technical challenges, establishing a production process is equally or even more important to the commercialization of Si-based anode materials. Such a process not only must be scalable with economic feasibility but also technologically robust to achieve optimal properties of the Si-based anode materials. Among the numerous production methods reported to date, magnesiothermic reduction reaction (MRR) remains a viable candidate for Si material production process. Since Bao and co-workers reported Si synthesis via thermal reduction of silicon oxide by magnesium (Mg),²⁸⁻³⁰ many Si-based anode materials synthesized from MRR has been reported.^{4, 31-}

³⁷ However, certain challenges still remain: Due to the exothermic nature of MRR, it is difficult to control the microstructure of the obtained Si due to the fusion of Si.³⁸ Generation of byproducts including magnesium silicate (Mg_2SiO_4) and magnesium silicide (Mg_2Si) is another severe challenge of MRR.³⁹⁻⁴⁰ These byproducts are induced due to discrepant atoms mobilities in Si-Mg-O system and the chemical stability of the interface between MgO, SiO_2 and Si.⁴¹ Finally, the kinetics of MRR is not well understood therefore it has been difficult to optimize the MRR process. In this work, we started with preparing the precursor from the commercial silica suspension in water (LUDOX HS-40) via a simple spray drying process, followed by a detailed investigation of the kinetics of the magnesiothermic reduction of the silica particles. From the kinetic study, porous Si particles with optimal conversion, microstructure, and electrochemical properties were produced. After carbon coating via chemical vapor deposition (CVD), the final product of the Si-C composite demonstrated superior performance as the Li-ion anode material under commercially relevant testing conditions.

2.2 Experimental Methods

2.2.1 Synthesis of Silicon-carbon

Commercial silica water suspension (LUDOX HS-40) was diluted with deionized water from 40 wt.% solid content to 20 wt.%. The obtained suspension was spray-dried with an industrial aerosol spray dryer at 150°C. The obtained spray-dried silica powder was thoroughly mixed with the magnesium (Mg) powder (300 mesh) with a molar ratio of $\text{Mg}:\text{SiO}_2=2.2:1$ under argon environment. In the MRR experiments with heat scavenger, sodium chloride (NaCl) with mass ratio $\text{Mg}:\text{NaCl}=1:1$ was added in the mixture. In a typical MRR, 2.7 g of the mixture was sealed in a stainless-steel reactor (5 mL) under argon. The reactor was heated in a tube furnace at 1°C min^{-1} from room temperature to the isothermal step temperature (580°C, 680°C, or 780°C). The isothermal step was 1h, 3h, 6h, 9h or 12h followed by natural cooling to room temperature. The obtained material was rinsed with 45 mL of 2 M HCl solution (H_2O : Ethanol= 1:1 by volume) for 12h to remove MgO and unreacted Mg, then 1 mL HF (49 wt.%) was added into the solution to remove unreacted silica. The resultant Si materials were washed with water and collected via filtration. Final products were dried in vacuum oven for 12h. Carbon coating was performed via CVD in a rotating tube furnace. In a typically CVD process, 1.0 g of Si was loaded in the tube reactor. After purging with Ar (100 sccm) for 60 min, the reactor was heated with a ramp rate of $10^\circ\text{C min}^{-1}$ to 700 °C. After reaching the temperature, acetylene

(C₂H₂) and argon gas mixture was introduced with flow rate C₂H₂/Ar=10/20 sccm while rotating the tube reactor. After certain time (depending on the targeted ratio of carbon coating), the acetylene feed was cut off and the reactor was naturally cooled down to room temperature.

2.2.2 Materials Characterizations

The crystalline compounds after MRR and after acid rinsing were analyzed by X-ray diffraction (XRD, PANalytical EMPYREAN) with a CuK α source. The morphology and microstructure of the Si and Si-C were analyzed by transmission electron microscopy (TEM, Tecnai 12) and scanning electron microscope (SEM, Nova NanoSEM 450). The surface area was measured from the N₂ adsorption and desorption isotherms with the Brunauer-Emmett-Teller (BET) method with an ASAP 2020 instrument. TGA was performed by a TA Instrument analyzer (Q 500) at ramp rate of 10 °C min⁻¹ from room temperature to 600 °C in dry air with a 60 min isothermal step at 600 °C.

2.2.3 Electrochemical Analysis

Electrochemical analyses were performed with two-electrode 2032-type coin cells. In the half cells to test the pure Si materials from MRR and the Si-C composites after carbon

coating, the working electrode was composed of 80 wt.% of Si (or Si-C), 10 wt.% of sodium carboxymethyl cellulose (CMC), and 10 wt.% of acetylene black. The typical areal loading of pure Si or Si-C was 1 mg cm^{-2} . The Si-C-graphite electrode was composed of 90 wt.% Si-C and graphite, 4 wt.% of CMC, 1 wt.% of styrene-butadiene, and 5 wt.% of acetylene black. The typical areal loading of Si-C and graphite was 4.1 mg cm^{-2} . The electrolyte was composed of Lithium hexafluorophosphate (LiPF₆) solution (1M) in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and fluoroethylene carbonate (FEC) (volume ratio EC: DEC: FEC = 45:45:10). Commercial lithium foil (750 μm thickness) is used as the counter electrode. Galvanostatic cycling was performed between 0.01 and 1.2 V vs Li/Li⁺ in half cells. The current density for Si and Si-C electrode was 100 mA g^{-1} . The current density for Si-C-graphite electrodes was 0.1 mA cm^{-2} at first cycle and then 0.5 mA cm^{-2} or 1.0 mA cm^{-2} for the subsequent cycles. In the full cell tests, the LiFePO₄ cathode was composed of 90 wt.% of LiFePO₄ powder, 5 wt.% polyvinylidene fluoride and 5 wt.% of acetylene black with typical areal loading of 20 mg cm^{-2} . The full cells were cycled between 2.0 V to 3.6 V with 0.5 mA cm^{-2} or 1.0 mA cm^{-2} current density. The full cells were charged with constant-current-constant-voltage method. The constant voltage was 3.6 with a cut-off current of 0.05 mA cm^{-2} .

2.3 Results and Discussion

Silica particles were first produced from an aerosol spray drying process illustrated in **Figure 2.1**.

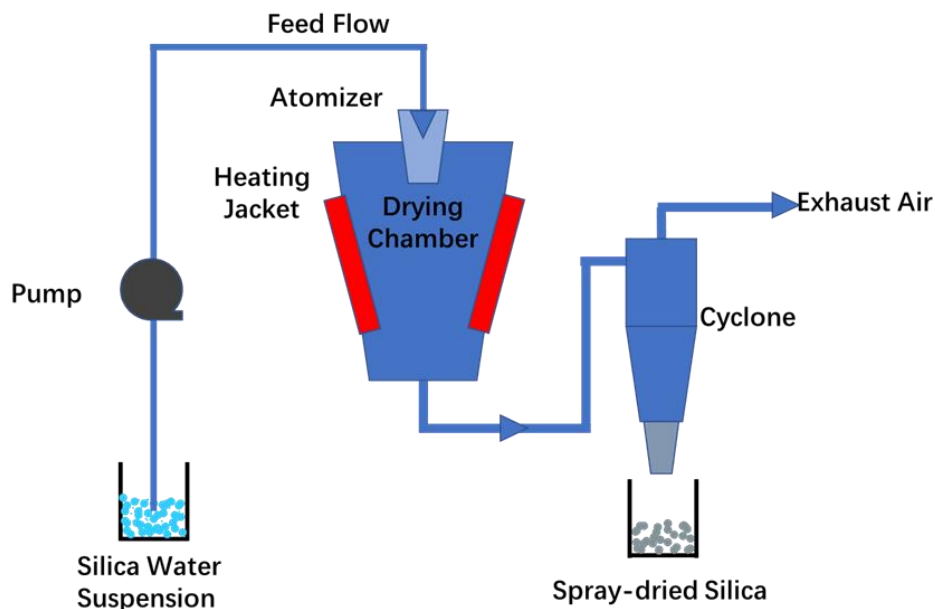


Figure 2.1 Schematic drawing of the industrial aerosol spray drying process.

In brief, commercial silica water suspension (LUDOX HS-40 with 40 wt.% silica content) was diluted with water and atomized with a two-fluid atomizer nozzle. The generated aerosol was carried into a stainless-steel dryer at 150°C by nitrogen gas to obtain the dried silica particles, of which the scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images are displayed in **Figure 2.2**. The average size of the silica particle is 11 μm as indicated by the particle size distribution in **Figure 2.2 (b)**. Each

particle is composed of many 10-nm primary silica particles [Figure 2.2 (c)], which is consistent with the particle size of silica in LUDOX HS-40.

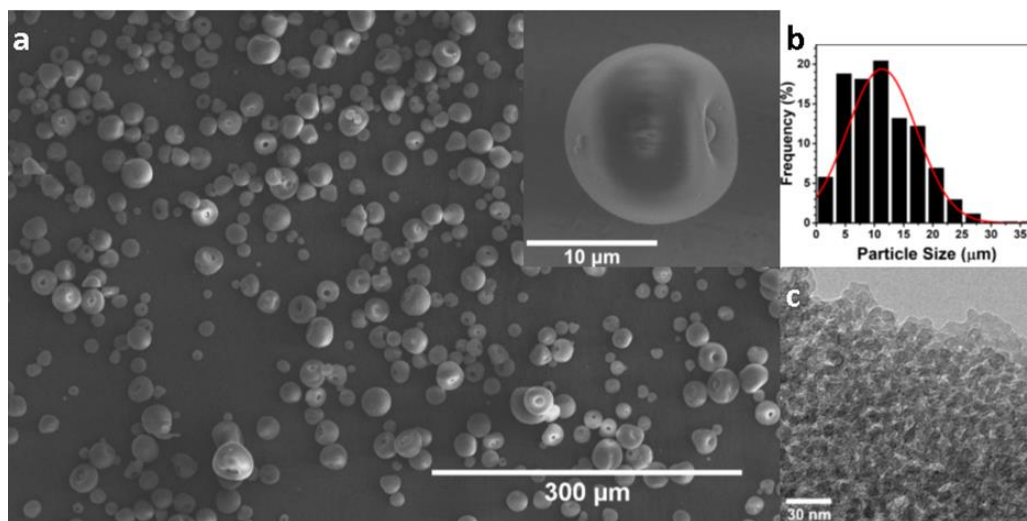


Figure 2.2 (a) SEM image of the silica particles obtained from aerosol spray drying (inset is a particle under high magnification); (b) silica particle size distribution; and (c) TEM image showing the primary silica particles.

The BET specific surface area of the silica particles is $178 \text{ m}^2 \text{ g}^{-1}$ measured from nitrogen adsorption-desorption isotherms (Figure 2.3).

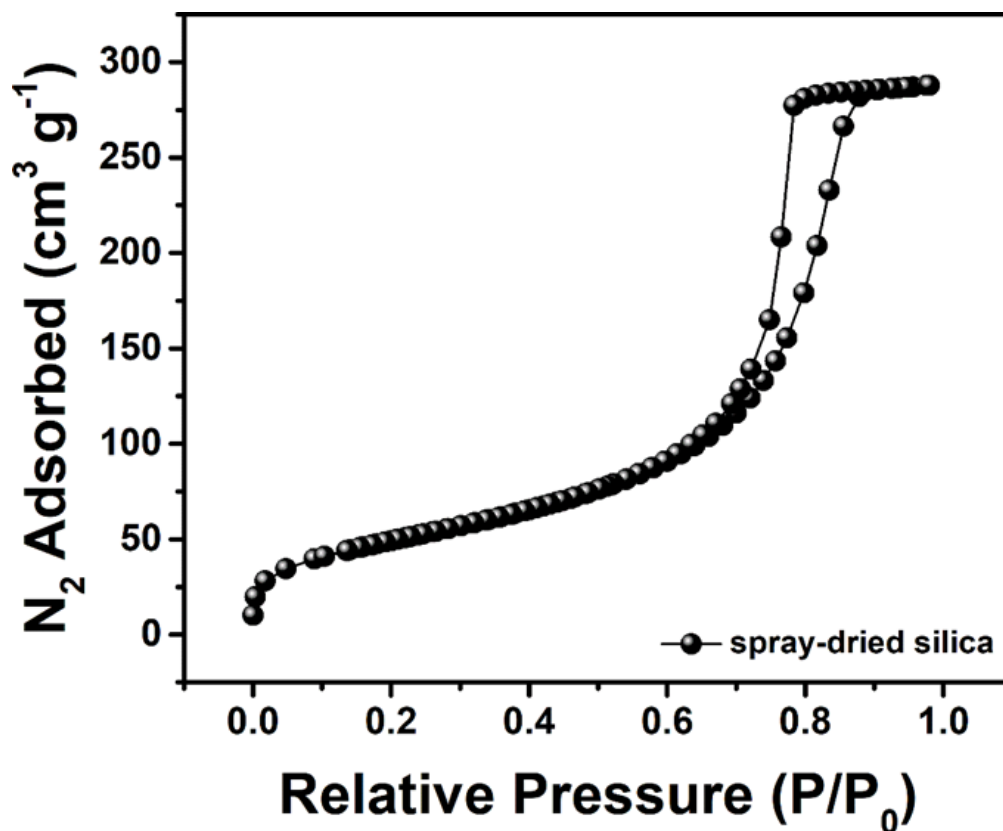


Figure 2.3 N_2 adsorption-desorption isotherms of the spray dried silica.

The obtained silica particles were subsequently reduced to Si via MRR process. The mixture of silica particles and Mg powder (300 mesh) was sealed in a home-made stainless-steel reactor under argon and the reactor was heated to $580^\circ C$ with a rate of $1^\circ C min^{-1}$. To measure the onset temperature of the MRR, a high-temperature thermocouple was inserted in the home-made stainless-steel reaction (the image of the reactor with the thermocouple is shown in **Figure 2.4**).

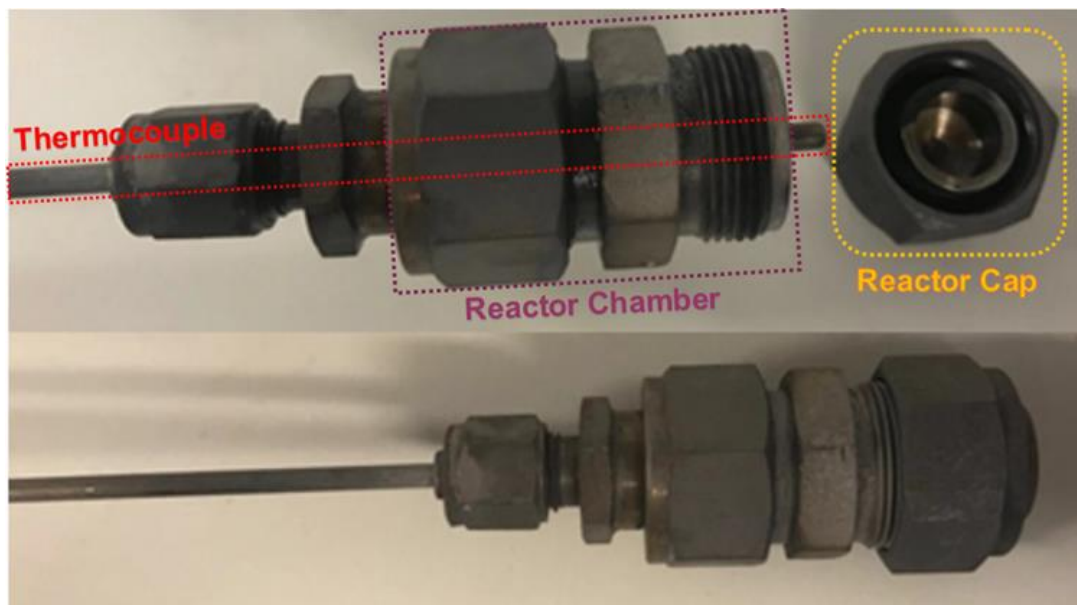


Figure 2.4 image of the MRR reactor with thermocouple inserted.

As shown in **Figure 2.5 (a)**, a temperature spike occurred at 538°C and the highest temperature recorded by the thermocouple is 1673°C. Although the temperature spike only lasted no more than 5 seconds (the heat was dissipated through the stainless-steel body of the reactor), it significantly undermined the quality of the product by forming a considerable amount of Mg_2Si due to the accelerated Mg diffusion in Si at high temperature.⁴¹⁻⁴²

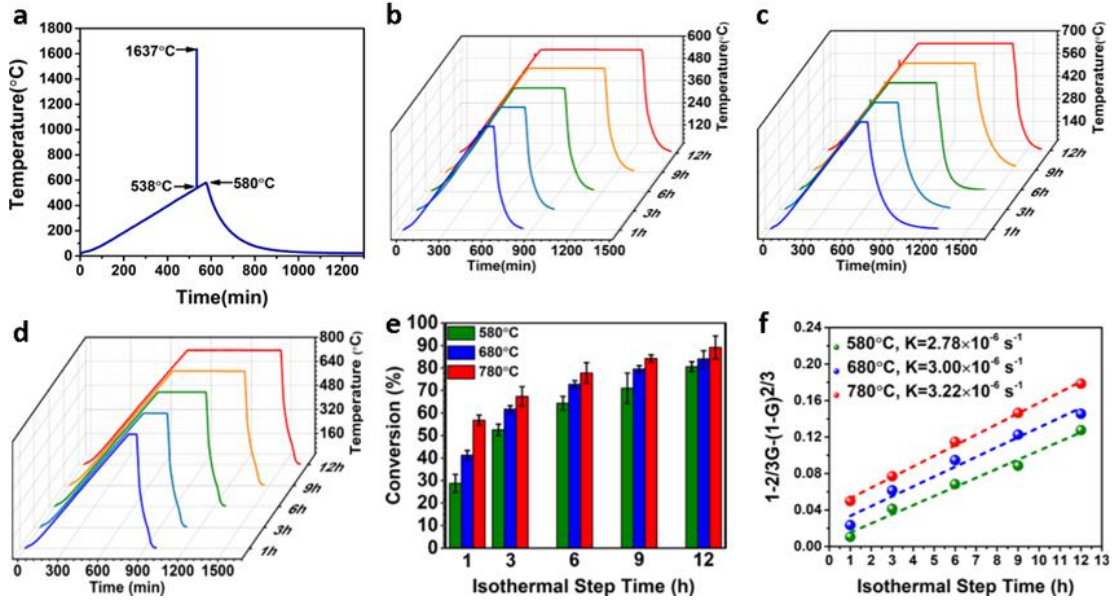


Figure 2.5 (a) Temperature profile of the MRR without NaCl in the reactant mixture of silica and Mg powder; Temperature profiles of MRR with NaCl as the heat scavenger (weigh ratio Mg:NaCl = 1:1) for isothermal step at (b) 580°C, (c) 680°C, and (d) 780°C with different isothermal step duration; (e) The silica-to-Si conversion under different reaction temperature and duration; (f) Ginstling-Brounshtein model fitting with the conversion data to obtain the reaction rate constant at different reaction temperature.

To alleviate the impact of this exothermic process, sodium chloride (NaCl) was added into the reactant mixture as the heat scavenger.⁴³⁻⁴⁴ With the addition of NaCl (mass ratio Mg:NaCl=1:1), MRR under different reaction (isothermal step) temperatures (580°C, 680°C and 780°C) and reaction durations (1h, 3h, 6h, 9h, and 12h) were performed. **Figures 2.5 (b)-2.5 (d)** show the temperature profiles in the reactor as the function of time. It is

clear that NaCl effectively absorbed the heat released by MRR thus no temperature spike was observed. The powder X-ray diffraction (XRD) pattern in **Figure 2.6 (a)** indicates that the products from MRR at 580°C contain magnesium oxide (MgO), Si and NaCl without indication of Mg_2Si or Mg_2SiO_4 byproducts. After rinsing the product with hydrochloric acid and hydrofluoric acid to remove NaCl, MgO and unreacted silica, the XRD pattern of the final product (**Figure 2.6 (b)**) indicates crystal Si.

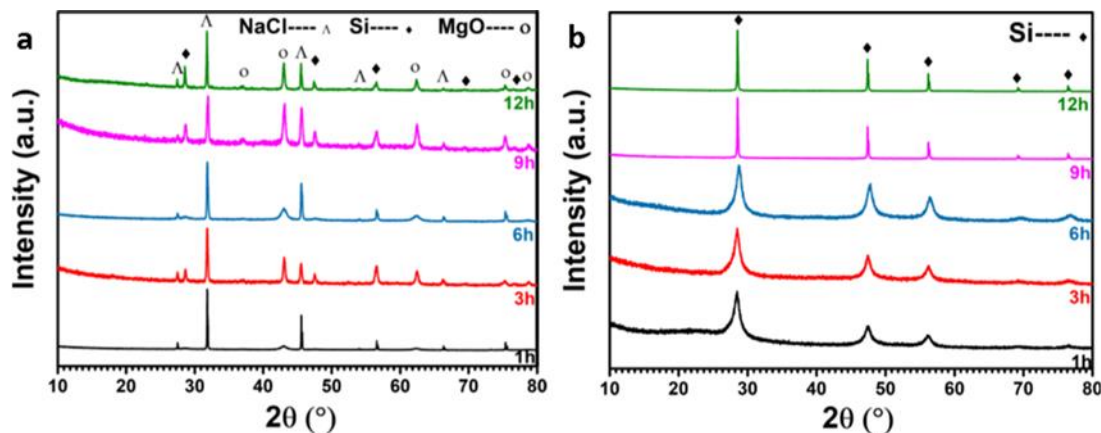


Figure 2.6. XRD patterns of (a) products from MRR at 580°C with NaCl (Mg:NaCl=1:1) for 1h, 3h, 6h, 9h and 12h and (b) products after rinsing with hydrochloric acid and hydrofluoric acid.

The silica-to-Si conversion at different reaction temperature and duration was also obtained as shown in **Figure 2.5 (e)**. As expected, the conversion (from triplicate experiments) increases with increasing reaction temperature and reaction duration. The conversion

results fit excellently to the Ginstling-Brounshtein model, which is a kinetics model for solid-state reaction under high yield condition: ⁴⁵⁻⁴⁶

$$kt = 1 - \frac{2}{3}G - (1 - G)^{\frac{2}{3}} \quad (1)$$

where k is the MRR rate constant, G is the conversion, and t is the isothermal step time. As shown in **Figure 2.5 (f)**, the MRR rate constant obtained from the fitting at 580°C, 680°C and 780°C is $2.78 \times 10^{-6} \text{ s}^{-1}$, $3.0 \times 10^{-6} \text{ s}^{-1}$ and $3.22 \times 10^{-6} \text{ s}^{-1}$, respectively. With the rate constants, the effective activation energy of the MRR (with NaCl as heat scavenger) in the temperature range 580 - 780°C is calculated as 5.5 kJ mol^{-1} . The low activation energy indicates the MRR is a mass transfer limited process. Furthermore, the silica-to-Si conversion can be predicated as a function of time with the reaction rate constants (**Figure 2.7**).

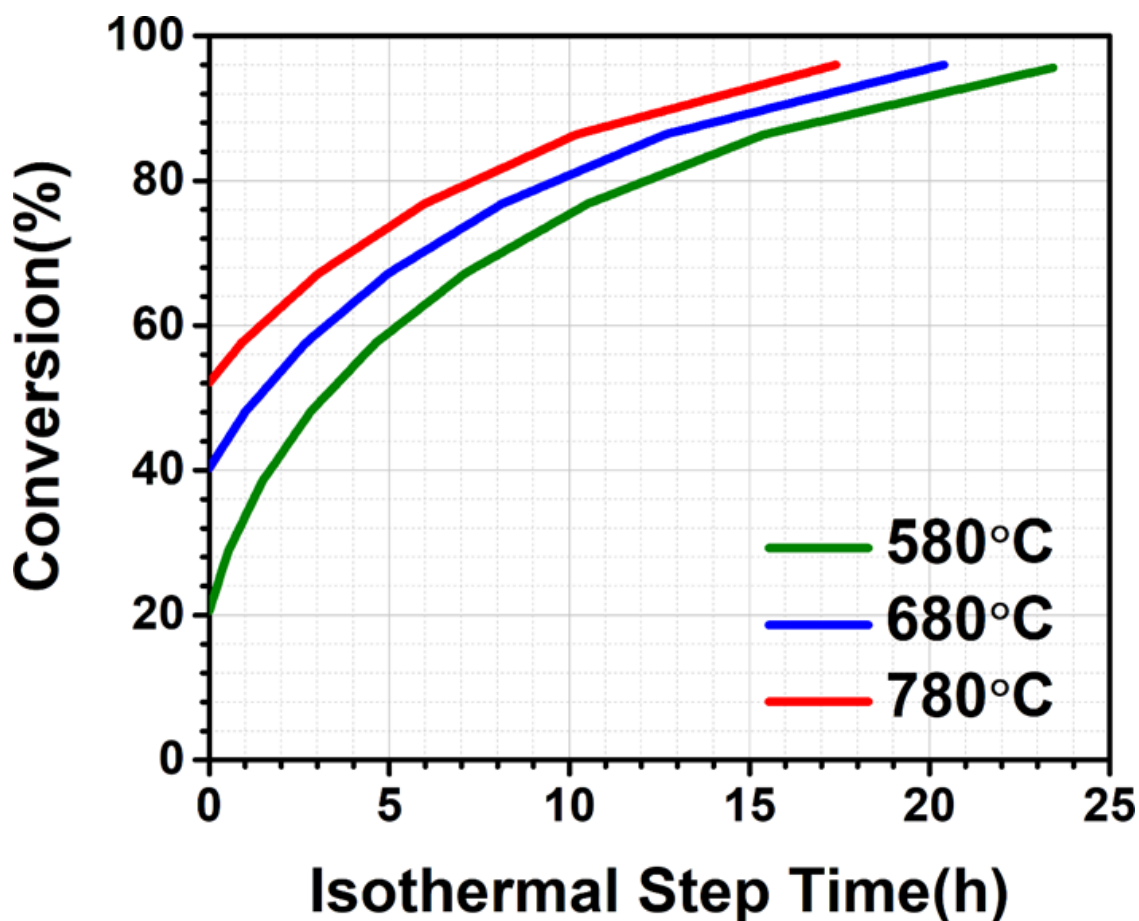


Figure 2.7. The prediction of the silica-to-Si conversion from MRR under our experimental condition.

The kinetics of the MRR (i.e., different reaction temperature and duration) not only affected the conversion, but also the microstructure of the obtained Si. The full width at half maximum of the XRD peaks of the Si produced at 580°C (**Figure 2.6 (b)**) indicates the size of the Si crystal grains grows with increasing reaction duration. This observation is confirmed by the TEM images of the Si displayed in **Figure 2.8**, which clearly illustrate

that the porosity of Si from MRR decreases monotonically with the increasing reaction duration. The specific BET surface area of these Si materials in **Figure 2.8 (f)** further confirms the finding: All Si from MRR at 580°C have lower specific surface area than that of the precursor silica particles ($178 \text{ m}^2 \text{ g}^{-1}$). Their specific surface area decreases from $113.8 \text{ m}^2 \text{ g}^{-1}$ (1 h reaction) to $22.6 \text{ m}^2 \text{ g}^{-1}$ (12 h reaction) monotonically with increasing reaction duration.

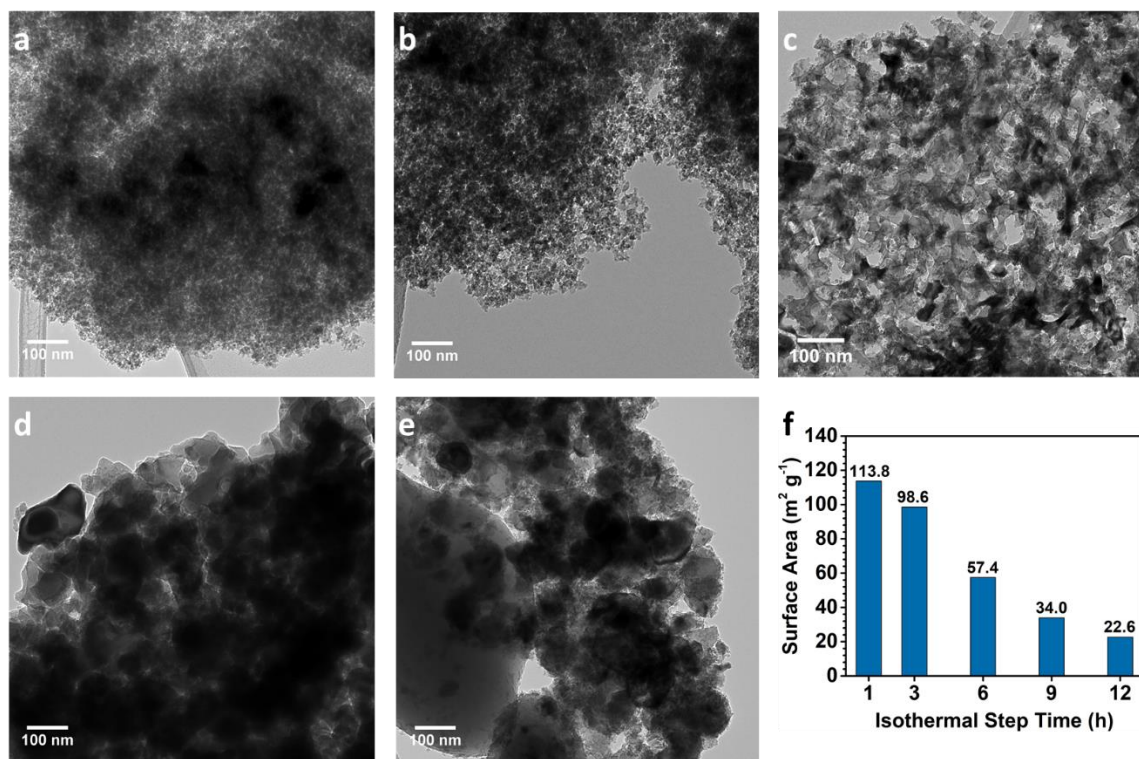


Figure 2.8. TEM images of the Si materials from MRR at 580°C with NaCl (Mg:NaCl=1:1) for isothermal step time of (a) 1h, (b) 3h, (c) 6h, (d) 9h and (e) 12h; (f) specific surface area of these Si from MRR at 580°C.

Si produced from MRR at 580°C were examined as the anode in half-cells with Li foil as the counter electrode. The electrode is composed of 80 wt.% of Si, 10 wt.% of sodium carboxymethyl cellulose (CMC) as binder, and 10 wt.% of acetylene black with a typical areal loading of 1 mg of Si per cm². **Figure 2.9 (a)** shows the cycle stability and Coulombic efficiency (CE) (from triplicate experiments) under lithiation-delithiation rate of 100 mA g⁻¹.

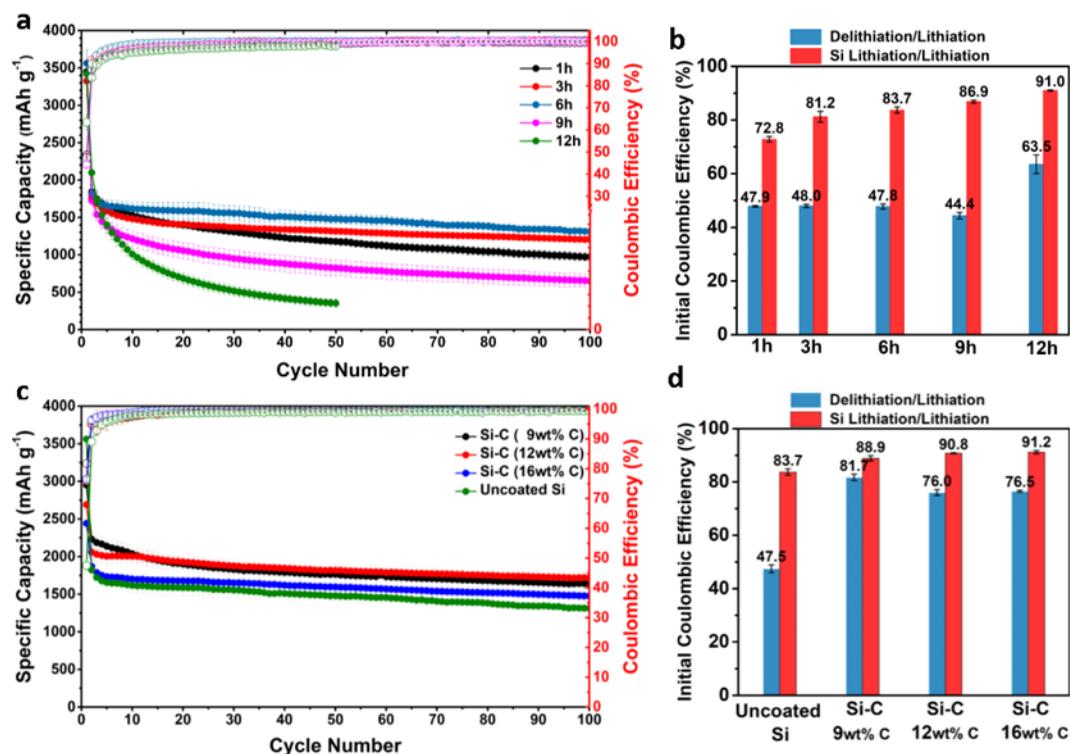


Figure 2.9 (a) Cycle stability and (b) ICEs of the Si materials produced from MRR at 580°C under different reaction duration; (c) Cycle stability and (d) ICEs of the Si from 6 h reaction duration after carbon coating via CVD. The lithiation-delithiation current is 100 mA g⁻¹.

The Si produced from 6 h reaction has the highest capacity retention: It delivered 3562 mAh g⁻¹ in the first lithiation and retaining 1344 mAh g⁻¹ capacity after 100 cycles. It is worth noting that there is a significant irreversible capacity between the 1st and 2nd lithiation in all electrodes, which leads to the low initial Coulombic efficiency (ICE). To better understand the origin of the low ICE, we calculated ICEs from two different methods as illustrated in **Figure 2.10** in Supporting Information.

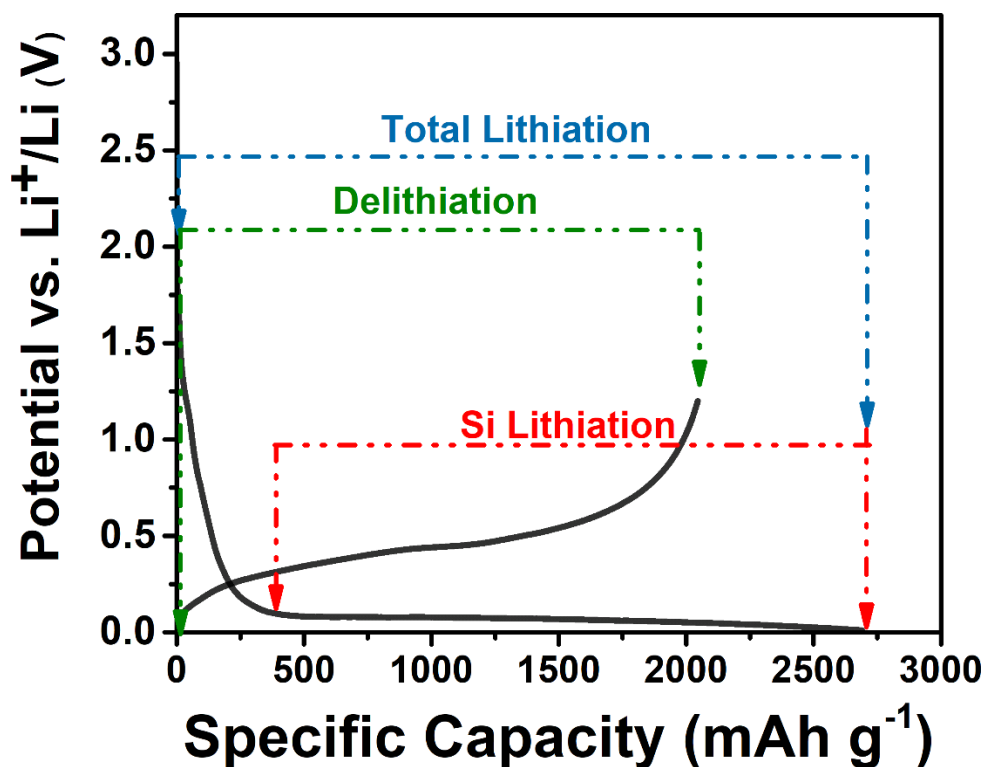


Figure 2.10 Lithiation-delithiation curve of pure Si anode illustrating the definition of the terms used in ICE calculation.

The first ICE (the conventional definition) is the ratio of delithiation capacity to the lithiation capacity; the second one is the ratio between the lithiation capacity attributed to Si (defined as the capacity below 0.13 V versus Li^+/Li) and the total lithiation capacity. As displayed in **Figure 2.9 (b)**, the ICEs based on the second method (red columns) are significantly higher than the conventional ICEs (blue columns): which means the low conventional ICE is clearly attributed to the irreversible capacity lost from delithiation of Si. The irreversibility can be attributed to the insulating nature of the Si and the worsened electronic contact induced by volume expansion.

Carbon coating has been proven an effective strategy to alleviate the challenges revealed above.⁴⁷⁻⁵² However, certain criteria of carbon coating have to be satisfied: The carbon coating should not promote undesired side reactions. Thus, carbon with intrinsic porous structure and rich functional groups containing heteroatoms (typically oxygen and nitrogen) is poor choice. Furthermore, the carbon coating needs to be conformal to not increase the accessible surface area and minimize the required amount of carbon. Based on these criteria, we selected chemical vapor deposition (CVD) as the carbon coating method in this study.⁵³⁻⁵⁷ Based on an overall consideration for optimal conversion, reaction temperature and duration, and cycle stability, Si from MRR at 580°C for 6 h was selected

for carbon coating. Si-C composites with different ratio of carbon coating of 9 wt.%, 12 wt.% and 16 wt.% (measured by thermogravimetric analysis in **Figure 2.11** were obtained via CVD using acetylene as the carbon source in a rotating tube furnace specifically designed by powder CVD process (MTI Corporation).

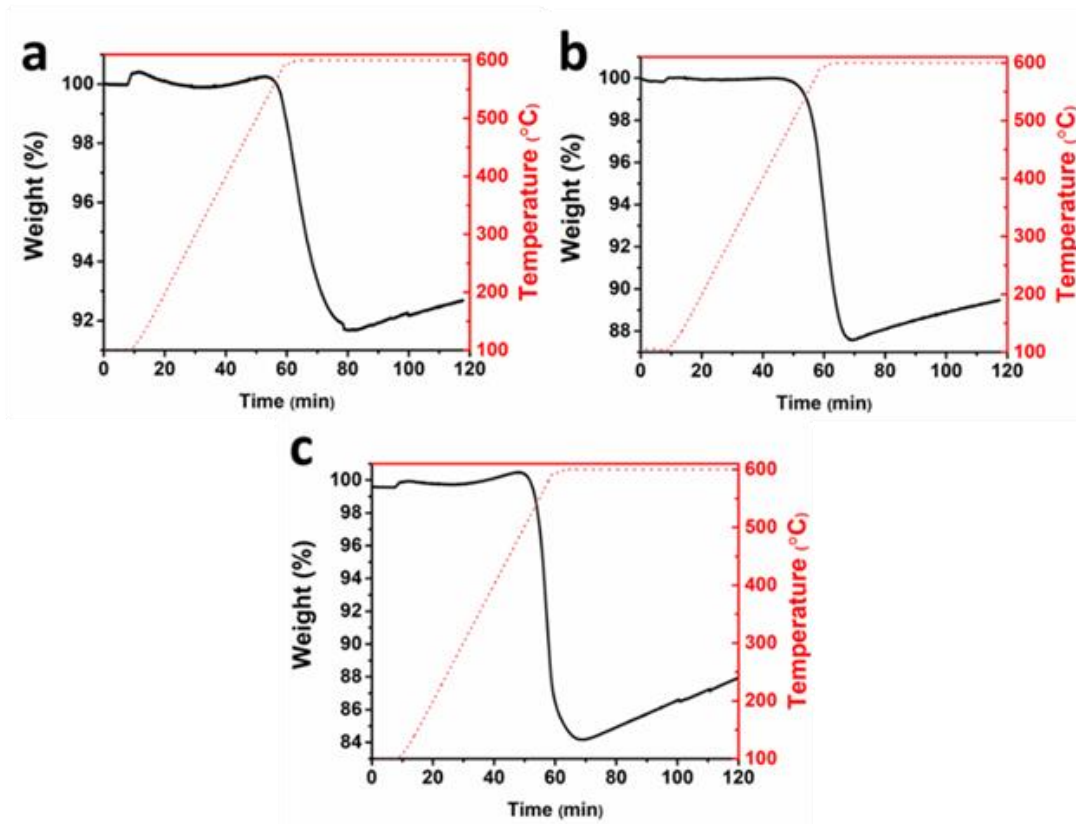


Figure 2.11 TGA curves of Si-C composite with carbon ratio of (a) 9 wt.%, (b) 12 wt.% and (c) 16 wt.%.

The cycle stability and ICEs from these Si-C composites are shown in **Figures 2.9 (c)** and **2.9 (d)**, respectively, in comparison with the uncoated Si. It is clear that the ICEs calculated from both methods are significantly improved. For the conventional ICE, it is improved from 47.5% (uncoated Si) to 81.7% (9 wt.% carbon), 76% (12 wt.% carbon), and 76.5% (16 wt.% carbon). High reversible capacity was also achieved with excellent cycle stability shown in **Figure 2.9 (c)**. The Si-C composite with 12 wt.% carbon demonstrates the best overall performance by considering ICE, capacity and cycle stability. Therefore, this Si-C composite was selected to be further examined as a drop-in material to the graphite anode.

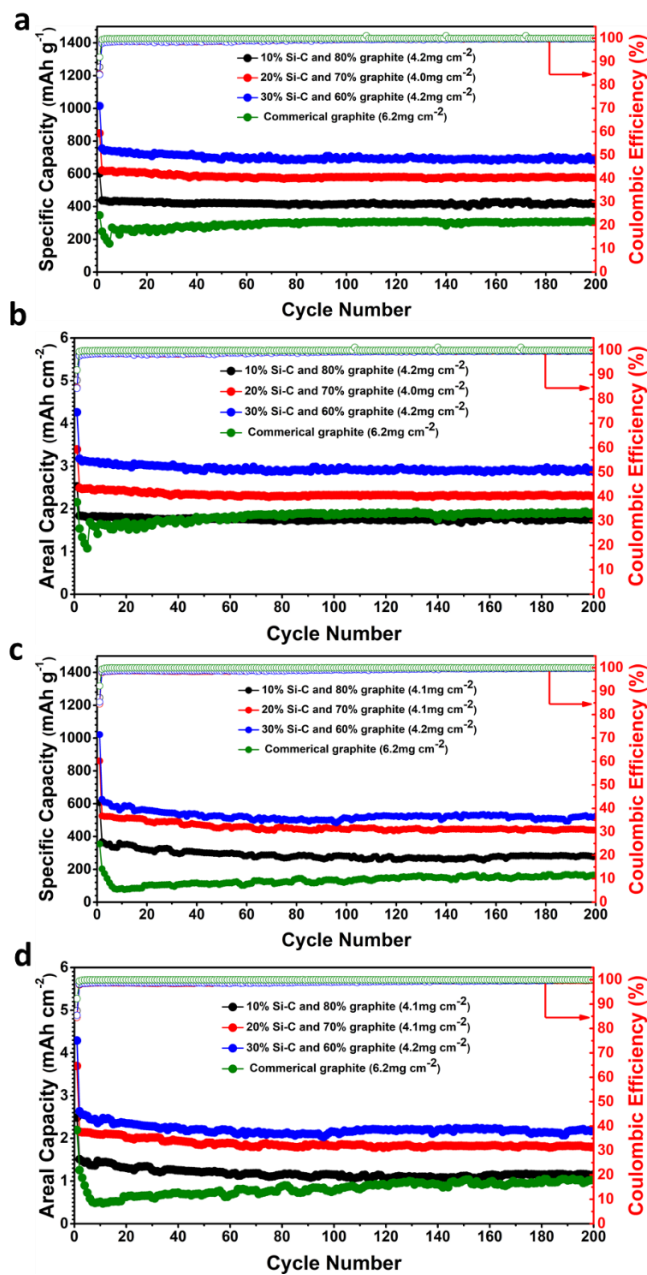


Figure 2.12 Specific capacity, areal capacity, cycle stability, and CE of the electrodes containing 10 wt.%, 20 wt.% and 30 wt.% Si-C composite in comparison with the pure graphite electrode at (a, b) 0.5 mA cm⁻² and (c, d) 1 mA cm⁻² lithiation-delithiation current. The first cycles are under 0.1 mA cm⁻².

The most practical application of Si-C composite is to be used as the drop-in additive in the graphite anode to enhance the capacity. In our testing, the Si-C composite was mixed with graphite at three different weight ratios: 10 wt.%, 20 wt.% and 30 wt.%. The corresponding graphite weight percentages are 80 wt.%, 70 wt. % and 60 wt.%. The other 10 wt.% of the electrode is composed of 4 wt.% of CMC, 1 wt.% of styrene-butadiene, and 5 wt.% of acetylene black. The total areal loading of Si-C and graphite was typically 4.1 mg cm⁻². **Figure 2.12** shows the specific capacity (based on the total mass of Si-C and graphite), area capacity, cycle stability and CE under current of 0.5 mA cm⁻² (Figure 6a and 6b) and 1.0 mA cm⁻² (Figures 6c and 6d). The first lithiation-delithiation cycle was carried under 0.1 mA cm⁻² for activation: the initial capacities of the electrodes with 10 wt.%, 20 wt.% and 30 wt.% of Si-C are 601 mAh g⁻¹ (2.5 mAh cm⁻²), 848 mAh g⁻¹ (3.4 mAh cm⁻²) and 1015 mAh g⁻¹ (4.3 mAh cm⁻²), respectively, superior to 347 mAh g⁻¹ (2.2 mAh cm⁻²) of the commercial graphite anode (areal loading 6.2 mg cm⁻²). The ICEs under 0.1 mA cm⁻² are 88% (10 wt.% Si-C), 85% (20 wt.% Si-C) and 84% (30 wt.% Si-C), which are slightly lower than that of the graphite anode (92%). After the cycling current was increased to 0.5 mA cm⁻² and 1.0 mA cm⁻², the electrodes containing Si-C composite still performed significantly better than the commercial graphite electrode as illustrated in Figure 6 and

summarized in **Table 2.1**. The representative lithiation-delithiation curves are shown in **Figure 2.13**.

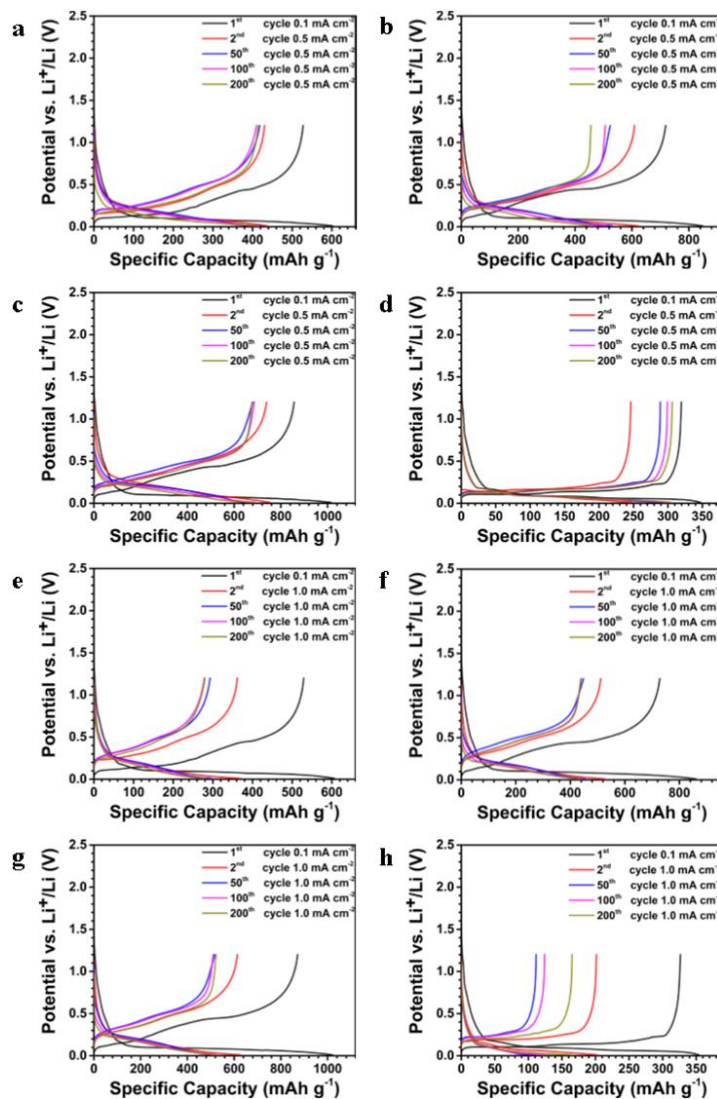


Figure 2.13 Representative lithiation-delithiation curves of electrodes containing (a) 10 wt.% Si-C and 80 wt.% graphite, (b) 20 wt.% Si-C and 70 wt.% graphite, (c) 30 wt.% Si-C and 60 wt.% graphite, and (d) 90 wt.% graphite with no Si-C at 0.5 mA cm^{-2} ; Representative lithiation-delithiation curves of electrodes containing (a) 10 wt.% Si-C and 80 wt.% graphite, (b) 20 wt.% Si-C and 70 wt.% graphite, (c) 30 wt.% Si-C and 60 wt.% graphite, and (d) 90 wt.% graphite with no Si-C at 1.0 mA cm^{-2} .

Table 2.1 Performance of the electrode composed of Si-C composite and graphite in comparison with the pure graphite electrode.

Electrode	1 st cycle Capacity (0.1 mA cm ⁻²)	ICE	0.5 mA cm ⁻²				1.0 mA cm ⁻²			
			2 nd Cycle Capacity	2 nd Cycle CE	Capacity retention 200 cycles	Average CE	2 nd Cycle Capacity	2 nd Cycle CE	Capacity retention 200 cycles	Average CE
10 wt.% Si-C	601 mAh g ⁻¹	88%	437 mAh g ⁻¹	98.3%	95%	99.5%	368 mAh g ⁻¹	98.1%	76%	99.4%
20 wt.% Si-C	848 mAh g ⁻¹	85%	622 mAh g ⁻¹	97.8%	92%	99.3%	526 mAh g ⁻¹	97.9%	84%	99.2%
30 wt.% Si-C	1014 mAh g ⁻¹	84%	756 mAh g ⁻¹	97.7%	90%	99.2%	626 mAh g ⁻¹	98.1%	84%	99.2%
Graphite	348 mAh g ⁻¹	92%	248 mAh g ⁻¹	99.4%	-	99.9%	202 mAh g ⁻¹	99.4%	81%	99.9%

The best all-around performance was demonstrated by the electrode containing 20 wt.% Si-C and 70 wt.% graphite: specific capacity and capacity retention are 622 mAh g⁻¹ (areal capacity 2.5 mAh cm⁻²) and 92% (after 200 cycles) at 0.5 mA cm⁻², and 526 mAh g⁻¹ (areal capacity 2.1 mAh cm⁻²) and 84% (200 cycles) at 1 mA cm⁻². To further demonstrate the relevant applications of the Si-C composite, we prepared the full cells (2032 coin cells) composed of the 20 wt.% Si-C anode and commercial lithium iron phosphate (LiFePO₄) cathode with controlled amount of electrolyte at 14 uL per cell, approximately 5.6 g Ah⁻¹. The full cells were cycled with constant-current discharge followed by constant-current-

constant-voltage (CCCV) charge with charge voltage at 3.6 V and cut off current at 0.05 mA cm⁻². **Figure 2.14 (a)** shows the cycle stability and CE of the full cell with specific capacity based on the total mass of Si-C and graphite. **Figures 2.14 (b)** and **2.14 (c)** display the representative cycling curves under current of 0.5 mA cm⁻² and 1.0 mA cm⁻², respectively. The initial capacities of the Si-C-graphite anode are 605 mAh g⁻¹ (2.4 mAh cm⁻²) under 0.5 mA cm⁻² and 485 mAh g⁻¹ (1.9 mAh cm⁻²) under 1 mA cm⁻². Capacity retentions after 200 cycles are 88% at 0.5 mA cm⁻² and 85% at 1 mA cm⁻².

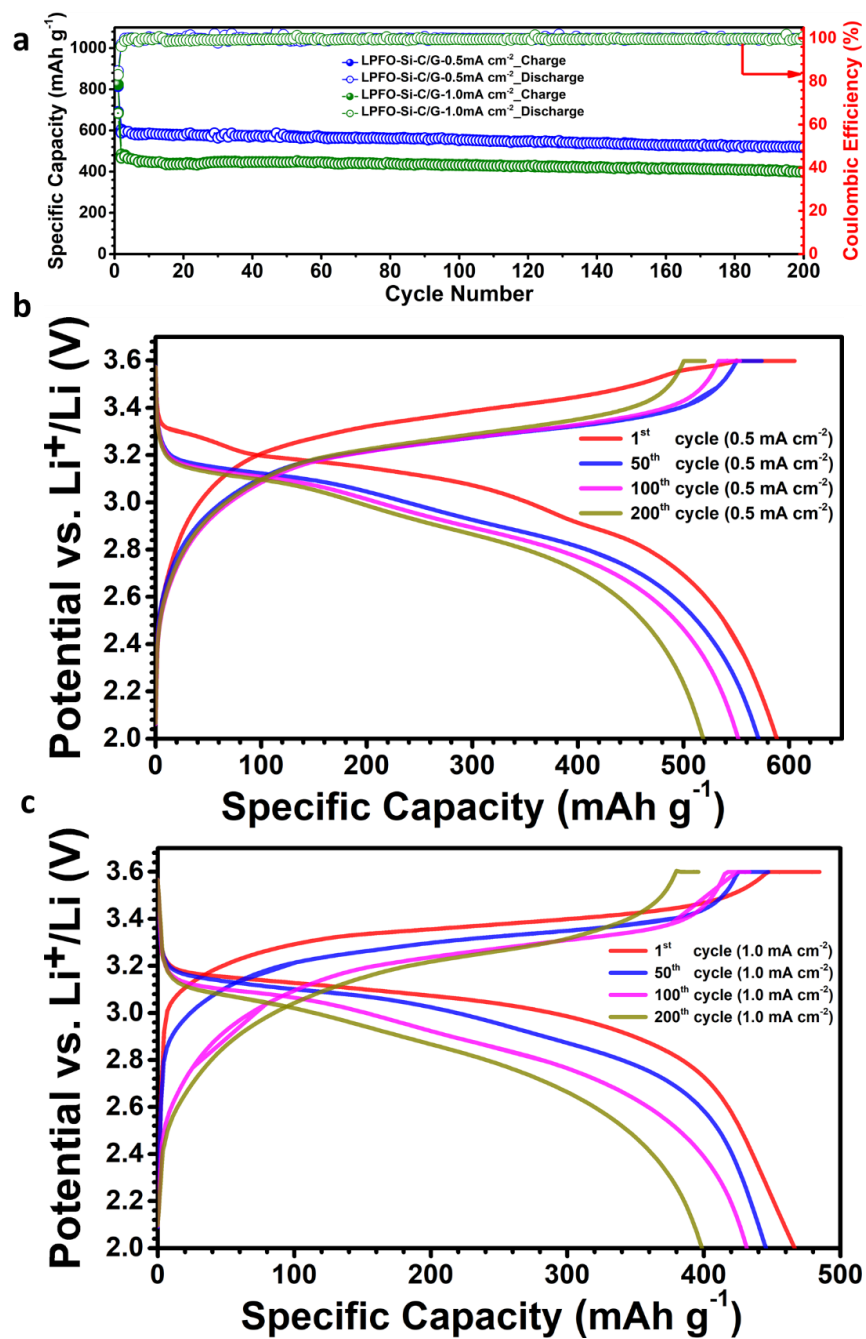


Figure 2.14 (a) Cycle stability of the Si-C-graphite/LiFePO₄ full cells under current of 0.5 mA cm⁻² and 1.0 mA cm⁻²; Representative charge and discharge voltage profiles under current of (b) 0.5 mA cm⁻² and (c) 1 mA cm⁻².

2.4 Conclusion

In summary, this chapter demonstrated an industrially feasible process to produce Si-C composites via magnesiothermic reduction of commercial silica and carbon coating via powder CVD. Through the kinetics study of the magnesiothermic reduction reaction, we obtained the key operational parameters to optimize the Si production. The produced Si-C composite materials demonstrated one of the best anode performances reported to date in open literature. We will continue to work on improving the initial Coulombic efficiency of the Si-C composite by refining the magnesiothermic reduction and carbon coating processes in our future investigations.

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Chapter 3. A Low Temperature Synthesis Graphitized Carbon Coated Silicon Anode Material

3.1 Abstract

This project reports a high-performance graphitized carbon silicon (Si-GC) composite anode material for Li-ion batteries via an energy efficiency and scalable production route. Porous Si was synthesized via magnesiothermic reduction followed by low temperature graphitized carbon coating. The Si-GC composite delivered an excellent specific capacity of 1195 mAh g⁻¹ and outstanding cycle stability. The thick electrodes with areal loading of 2.7 mg cm⁻² achieve remarkable performance: 917 mAh g⁻¹ overall specific capacity and 2.5 mAh cm⁻² areal capacity as well as 84% capacity retention after 200 cycles. Full cells composed of commercial lithium iron phosphate cathode and the Si-GC anode under lean electrolyte condition also demonstrate excellent performance.

3.2 Introduction

Graphite has been commercializing and grabbing market share as an anode material of Li-ion batteries for decades, because of its good electrochemical stability and resource accessibility.¹⁻³ But the theoretical capacity of 372 mAh g⁻¹ is lagging the nowadays

demand.⁴⁻⁷ With development of cathode materials such as high nicked content lithium nickel manganese cobalt oxide (NMC)⁸⁻⁹ or lithium sulfide (Li₂S)¹⁰⁻¹², low specific capacities anode materials once again become limitations. Currently the promising candidate Si has been drawn significant attentions and extensively studied and regarded as potential for lithium-ion (Li-ion) batteries application because of its terrifically high gravimetric and volumetric capacity.¹³⁻¹⁶ However, the unremitting volume change of Si results in solid-electrolyte-interphase continually breaking and reforming end up with incessantly consuming electrolyte and capacity fading.^{5, 17-18} Nowadays, the to solve the weakness of both materials are separated. In order to improve the specific capacity of graphite, some study has been conducted. For instance, carbon coated CoO hybrids¹⁹, carbon coated Co₃O₄²⁰ and One-dimensional carbon/Fe₃O₄ nanocomposite²¹. However, these transition metal materials have much higher lithiation/delithiation plateaus than those of graphite which offset the higher specific capacity in practical application of Li-ion batteries. For decades, tremendous works have been done to optimize the performance of Si anode materials, such as sandwich-structured Si nanoparticles,²²⁻²⁴ pomegranate-like Si-C,²⁵ yolk-shell Si-C²⁶⁻²⁸ and carbon coated Si.^{4, 28-30} All of them achieved impressive performances. However, the primary nanosized silicon usually been synthesized via liquid chemical method or chemical vapor deposition using silicon (IV) chloride (SiCl₄) or pyrophoric silane (SiH₄), which is costly, non-environmentally friendly and unscalable,

limiting the commercial application.³¹⁻³³ Magnesiothermic reduction reaction (MRR) has gained attention since Bao and co-workers reported that SiO_2 can be reduced by Mg and regraded as a promising synthesis method for Si.³⁴ It is inexpensive, high scalable. Many studies had been conducted and reported that Si materials reduced by Mg exhibited good electrochemical performance.³⁵⁻⁴²

In order to address the drawbacks of both Si and graphite to achieve high specific capacity and good cycle stability. In this work, we adopt a graphitic carbon coated on the porous Si surface.

Si acquired from MRR, porous nanostructure alleviated the volume change and avoid particle pulverization as well as provided good reversible capacity as high as 1800 mAh g^{-1} and relatively good cycle stability. Graphitic carbon coating not only created a layer to stabilize the Si SEI and buffer the volume expansion of Si, but also a good Li ion and electron conductivity medium.

3.3 Experimental Methods

3.3.1 Synthesis of Silicon-Graphitic Carbon

For synthesis Si precursor, commercial SiO_2 water suspension (LUDOX[®] HS-40 colloidal silica, particle size 10~15 nm) was diluted with deionized water then spray-dried with a

customized aerosol spray dryer at 120°C. 270 mg Si precursor was thoroughly mixed with the magnesium (Mg) powder (300 mesh) and sodium chloride (NaCl) with molar ratio of Mg/SiO₂/NaCl=2.2:1:1.37 in argon (Ar) filled environment for 1 hour. Then mixture was transferred and sealed in a stainless-steel reactor with Ar protection. The reactor was slowly ramp rate of 1°C min⁻¹ from room temperature to 600°C for 6 hours in a tube furnace. After cooling down to room temperature, the as-synthesized Si was treated with 45 mL HCl solution (2 mol; H₂O: Ethanol= 1:1 by volume) for 12h to remove MgO, then adding in 1 ml HF (49 wt.%) the solution to remove unreacted SiO₂. The resulting Si materials were washed and collected via vacuum filtration with 250 ml distilled water and 250 ml ethanol. Then Si were dried in vacuum oven for at least 12h. Afterwards, 1000mg glucose and graphitization catalyst 338/675 mg Fe (NO₃)₃ · 9H₂O dissolved in 10 ml H₂O/Ethanol (1:1 by volume) solution then added in different amount of porous Si (100/200 mg), heated up to 55°C and stirred for 2 hours then transfer to vacuum dryer under the temperature of 80 °C for 1 hour. Then transfer the syrup to ceramic boat and heat up at the rate of 3°C/min to 1000°C and held for 3 hours. Then as-synthesized Si-GC was washed with 45 mL HCl solution (2 mol; H₂O: Ethanol= 1:1 by volume) for 24h with sonication to remove iron species. Followed with wash and vacuum filtration and dry exactly same as collecting porous Si.

3.3.2 Materials Characterizations

The crystalline compounds porous Si and Si-GC were analyzed by X-ray diffraction (XRD, PANalytical EMPYREAN) with a $\text{CuK}\alpha$ source. The morphology and microstructure of the Si-GC were analyzed by transmission electron microscopy (TEM, Tecnai 12) and scanning electron microscope (SEM, Nova NanoSEM 450). The surface area was measured from the N_2 adsorption and desorption isotherms with the Brunauer-Emmett-Teller (BET) method with an ASAP 2020 instrument. TGA was performed by a TA Instrument analyzer (Q 500) at ramp rate of $10^\circ\text{C min}^{-1}$ from room temperature to 600°C in dry air with a 60 min isothermal step at 600°C .

3.3.3 Electrochemical Analysis

Electrochemical measurements were performed with two-electrode CR2032 coin-type cells. In the half-cells, the working electrode was composed of 80 wt.% of the Si-GC, 10 wt.% of sodium carboxymethyl cellulose (CMC) as binder, and 10 wt.% of acetylene black (Super-P). The typical thin electrode the areal loading was 0.5 mg cm^{-2} and above 2.7 mg cm^{-2} for thick electrode. The electrolyte was composed of Lithium hexafluorophosphate (LiPF_6) solution (1M) in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) (volume ratio of EC: DEC = 50:50). And commercial lithium foil ($750 \text{ }\mu\text{m}$ thickness) was used as the counter electrode with porous polypropylene separator. Cyclic

voltammetry (CV) was conducted on the half-cells with a scan rate of 0.1 mV s^{-1} in between 0.1 and 1.2 V vs Li/Li⁺. Galvanostatic cycling was performed between 0.01 and 1.2 V vs Li/Li⁺ with a current density of 100 mA g^{-1} for Si-GC thin electrode; For Si-GC thick electrode, 0.1 mA cm^{-2} at first cycle and then 0.5 mA cm^{-2} and 1.0 mA cm^{-2} applied to the subsequent cycles. In the full-cells tests, LiFePO₄ cathode was composed of 90 wt.% of LiFePO₄ powder, 5 wt.% polyvinylidene fluoride and 5 wt.% of acetylene black with typical areal loading of $\sim 20 \text{ mg cm}^{-2}$. LiFePO₄-Si-GC full cell was performed Galvanostatic cycling between 2.0 V to 3.8 V and using constant-current-constant-voltage charging method (CCCV) with a cut-off current of 0.05 mA cm^{-2} . The current densities were 0.1 mA cm^{-2} at first cycle and then 0.5 mA cm^{-2} and 1.0 mA cm^{-2} for the rest of cycles.

3.4 Results and Discussion

In brief, silicon (Si) precursor was produced via aerosol spray drying commercial silica (SiO₂) water suspension. Followed with magnesiothermic reduction reaction and acidic treatment producing porous Si, subsequently mixed with glucose and Fe (NO₃)₃ · 9H₂O to produce Si-GC via polymerization, carbonization and graphitization and acidic treatment. The process shows in **Figure 3.1**.

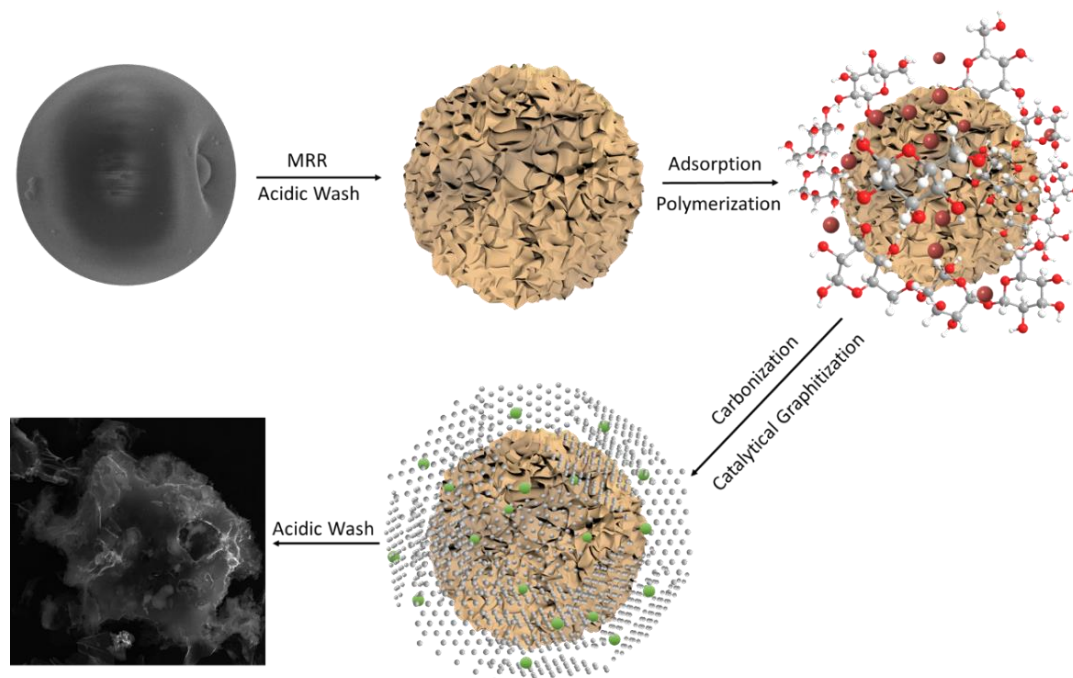


Figure 3.1 Fabrication process from spray-dried SiO₂ to Si-GC.

The morphologies of silica particles and spray-dried silica are shown in **Figure 3.2**.

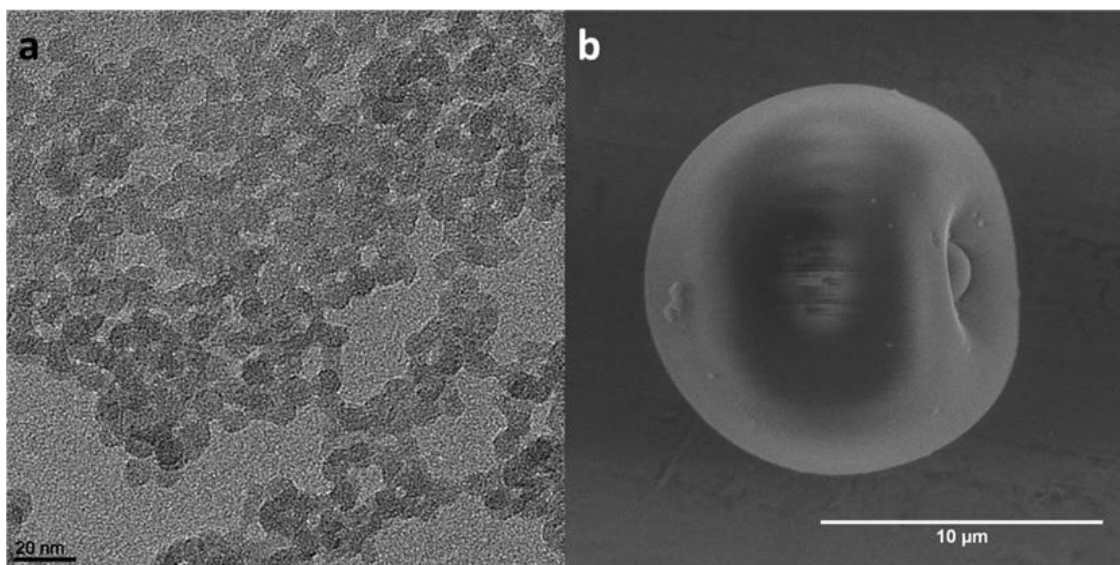


Figure 3.2 (a) TEM image of commercial SiO₂ particles; (b) SEM image of spray-dried SiO₂ particles.

The morphology of porous Si from magnesiothermic reduction of spray-dried SiO₂ was investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) and the results presented in **Figure 3.3**.

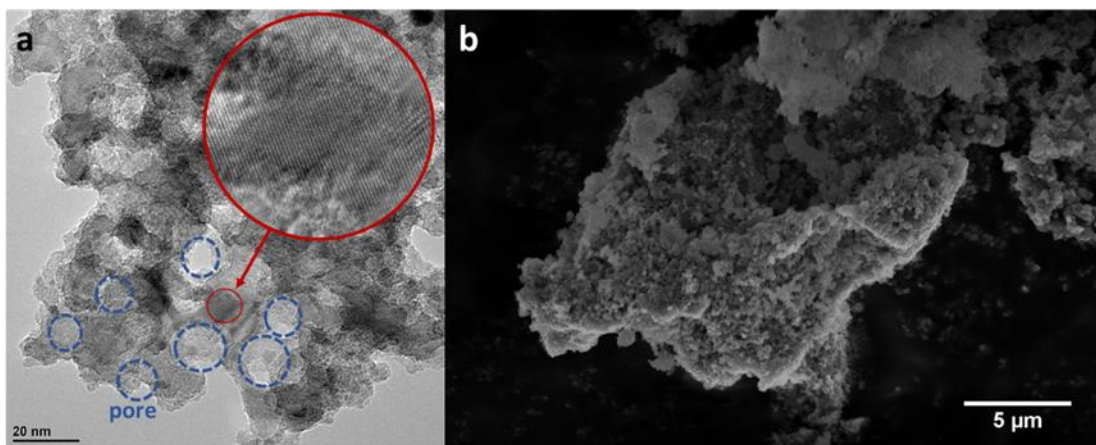


Figure 3.3 (a) TEM image of porous Si from magnesiothermic reduction of SiO₂ showing the primary Si particles and porous structure and inset is high magnification of Si particle; (b) SEM image of porous Si.

The BET specific surface area of the porous Si is 57.4 m² g⁻¹ measured from nitrogen adsorption-desorption isotherms. The powder X-ray diffraction (XRD) pattern in **Figure 3.4** (a) shows the trace of magnesium oxide (MgO), Si and NaCl after MRR at 600°C for 6 hours. After treating the product with HCl and HF then rinsing with H₂O and ethanol to remove MgO, unreacted SiO₂ and NaCl, the final product is proven by a crystal Si phase XRD pattern.

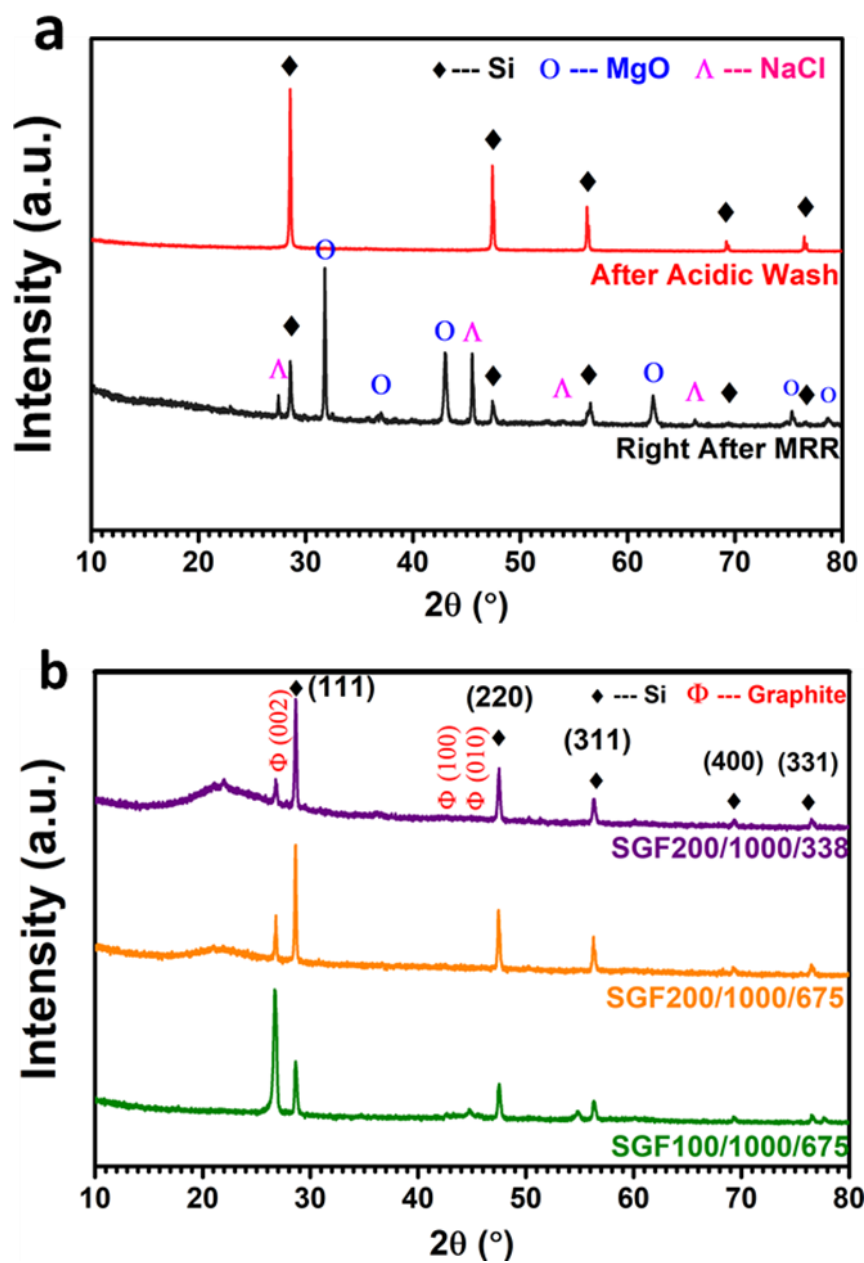


Figure 3.4 (a) XRD patterns of porous Si after magnesiothermic reduction and after acidic treatment; (b) XRD patterns of graphitized carbon coated Si with different glucose/ Fe^{3+} and Glucose/Si ratio.

The obtained porous Si was subsequently mixed with glucose and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in H_2O /Ethanol solution, when heated up the composite, the glucose started polymerizing. Si particles and Fe^{3+} were gradually impregnated by polycarbonate. Fe species was embedded as low temperature graphitization catalyst. After acidic treatment removing Fe species. The Si-GC was obtained. The XRD recorded the formation of crystalized graphitic carbon as well as existence of Si. **Figure 3.4** (b) shows the diffraction peaks of different glucose/ Fe^{3+} and Glucose/Si ratio Si-C (SGF). For instance, the denotation of SGF200/1000/338 can be interpreted as 200mg porous Si mixed with 1000 mg glucose and 338 mg $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The plane (002) and plane (010) at $\sim 26^\circ$ degree and $\sim 45^\circ$ degree which indicate the formation of graphitized carbon. Meanwhile the diffraction peaks of plane (111), (220), (311), (400) and (331) were match with porous Si.

The morphologies of different SGF ratio are displayed in **Figure 3.5**. **Figure 3.5** (a) is TEM showing the SGF100/1000/675 is composed of large solid particles cover with translucent few layers of sheet-like structure which indicates higher degree of graphitization corresponding with the XRD pattern. **Figure 3.5** (b) is SEM displaying the macrostructure of SGF100/1000/675 and **Figure 3.5** (c) and **3.5** (d) is EDS mapping of C and Si element, which demonstrate uniform graphitic carbon coating. With different SG ratio, less Si promotes the degree of graphitization. Compared **Figure 3.5** (a) and **3.5** (e) the TEM show

more graphitic carbon characteristics. Compared to SGF200/1000/675, with 1/2 amount of graphitization catalyst, **Figure 3.4** (b) shows the aspect ratio of characteristic peak of planes (002) (010) of typical hexagonal symmetry become weaker by using plane (111) of Si as reference which indicate less Fe catalyst reduce the degree of graphitization.

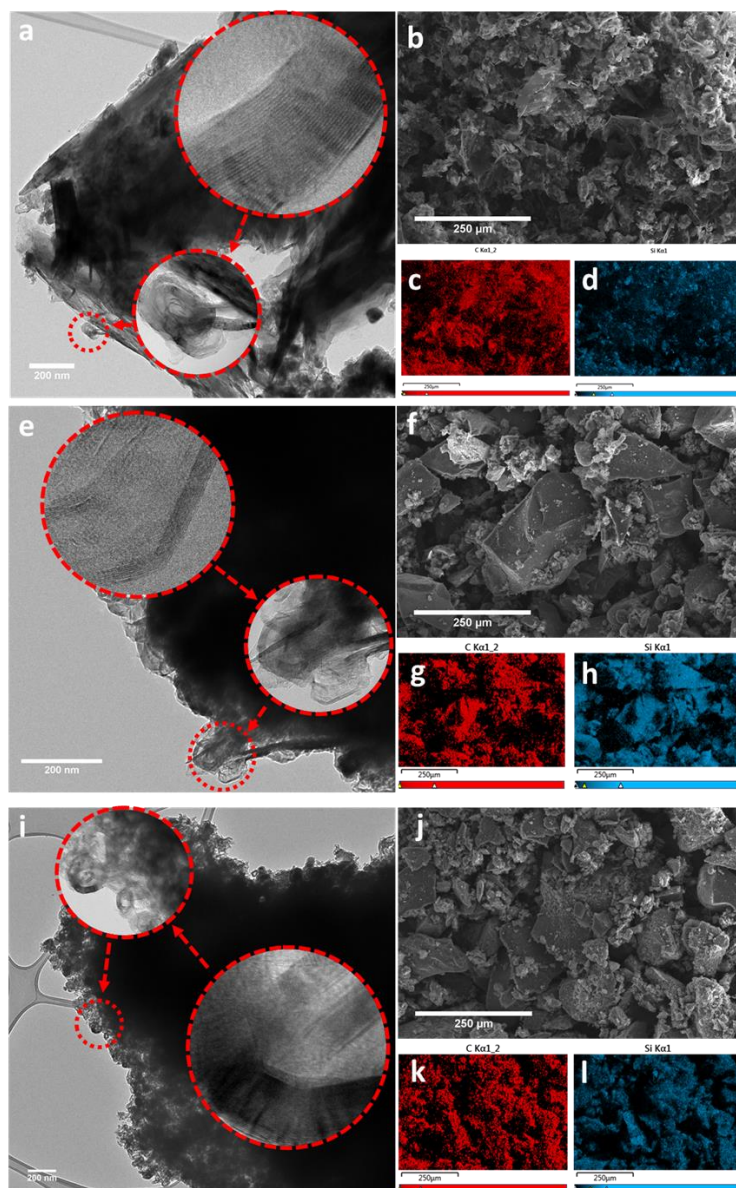


Figure 3.5 (a) TEM image of SGF100/1000/675; (b) SEM image of SGF100/1000/675; (c-d) EDS mapping of element C and Si of SGF100/1000/675; (e) TEM image of SGF100/1000/675; (f) SEM image of SGF200/1000/675; (g-h) EDS mapping of element C and Si of SGF200/1000/675; (i) TEM image of SGF100/1000/338; (j) SEM image of SGF200/1000/338; (k-l) EDS mapping of element C and S of SGF200/1000/338.

Si-GC produced from low temperature graphitization was tested in half cell. The electrode was made of 80 wt.% of Si-GC, 10 wt.% of sodium carboxymethyl cellulose (CMC) and 10 wt.% of acetylene black with areal loading of $\sim 0.5 \text{ mg cm}^{-2}$. **Figure 3.6** (a) and (b) show the coulombic efficiency (CE) and cycle stability (from triplicate cells), the lithiation and delithiation current density is 100 mA g^{-1} .

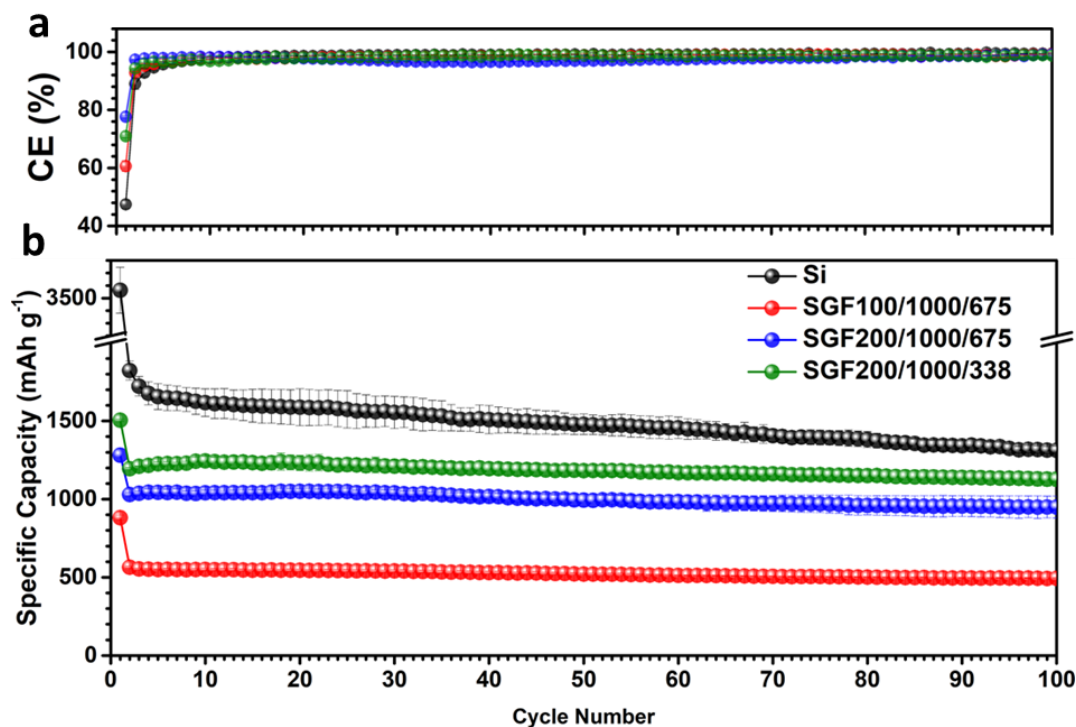


Figure 3.6 (a) coulombic efficiency and (b) cycle stability of porous Si and Si-GC at current density of 100 mA g^{-1} .

Although porous Si deliver highest specific capacity of 3562 mAh g⁻¹ in the first lithiation, the bad initial coulombic efficiency (ICE) ~48% displays significant irreversibility indicate at the beginning of cycle life would consume large amount electrolyte and formation of thick SEI layer, with lean electrolyte, the poor ICE will defiantly hint the practical application of porous Si. Coating a carbon layer on Si surface has been demonstrated an effective way to accommodate volume change and stabilized the SEI.

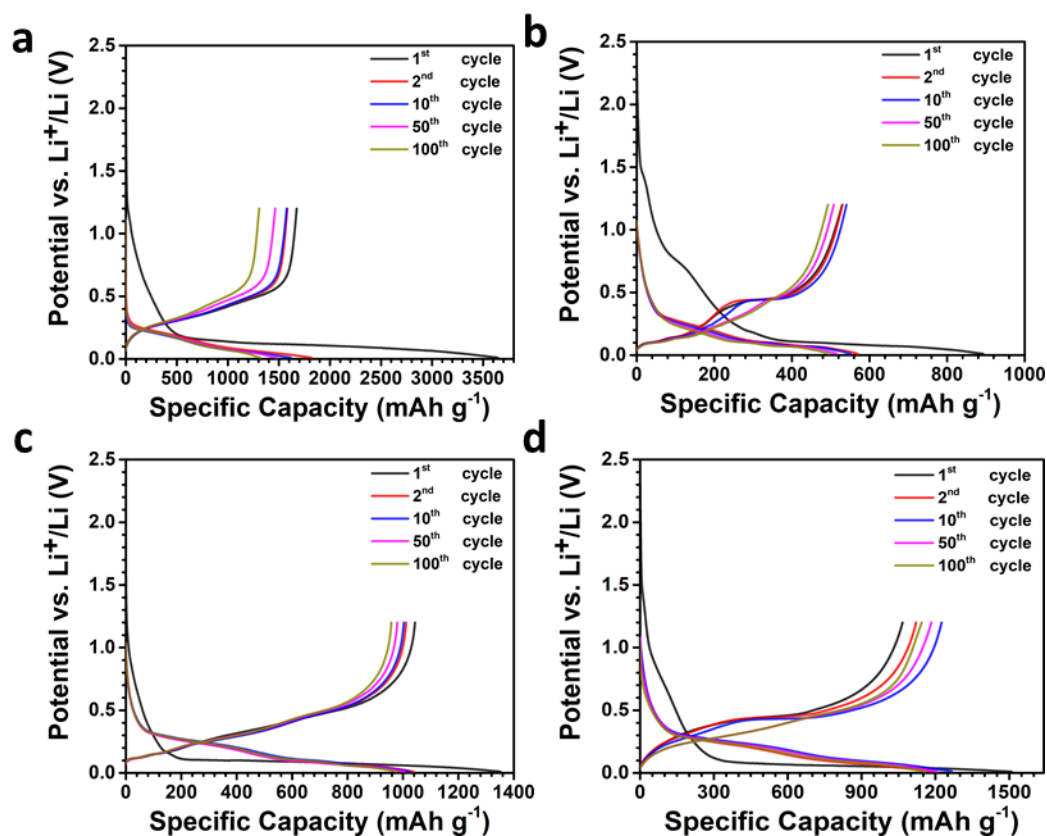


Figure 3.7 Representative charge and discharge voltage profiles under current density of 100 mA g⁻¹.

Unlike the conventional carbon coating, graphitic carbon coating not only create a rigid buffer layer, but also graphitized carbon can restore Li ions to contribute specific capacity. SGF200/1000/675 shows the best electrochemical performance. At first lithiation, it delivers 1195 mAh g⁻¹ at 2nd cycle and retaining 1127 mAh g⁻¹ after 100 cycles. The ICEs were significantly improved as well as cycle stability. Details shows in **Table 3.1**.

	1st Lithiation Capacity (mAh g⁻¹)	ICE (%)	Capacity Retention (%, vs. 2nd Lithiation Capacity)
Porous Si	3562	47.5	72.0
SGF100/1000/675	882	60.6	87.4
SGF200/1000/675	1281	77.6	92.2
SGF200/1000/338	1504	70.9	94.3

Table 3.1 electrochemical performance of porous Si and Si-GC.

Areal capacity of any electrode lower than 2 mAh g⁻¹ is unconvincing and hard to meet ever-increasing commercial demand.¹⁵⁻¹⁶ Thick Si-GC electrodes were made. The electrodes were composed of 80 wt.% of Si-GC, 10 wt.% of sodium carboxymethyl cellulose (CMC) as binder and 10 wt.% of acetylene black. **Figure 3.8** exhibits the cross-section of Si-GC thick electrode, the thickness is around 50 μm for SGF100/1000/675 with

areal loading of around 4.6 mg cm^{-2} , $27 \text{ }\mu\text{m}$ for SGF200/1000/675 with areal loading of around 3.4 mg cm^{-2} , $21 \text{ }\mu\text{m}$ for SGF200/1000/338 with areal loading of around 2.7 mg cm^{-2} .

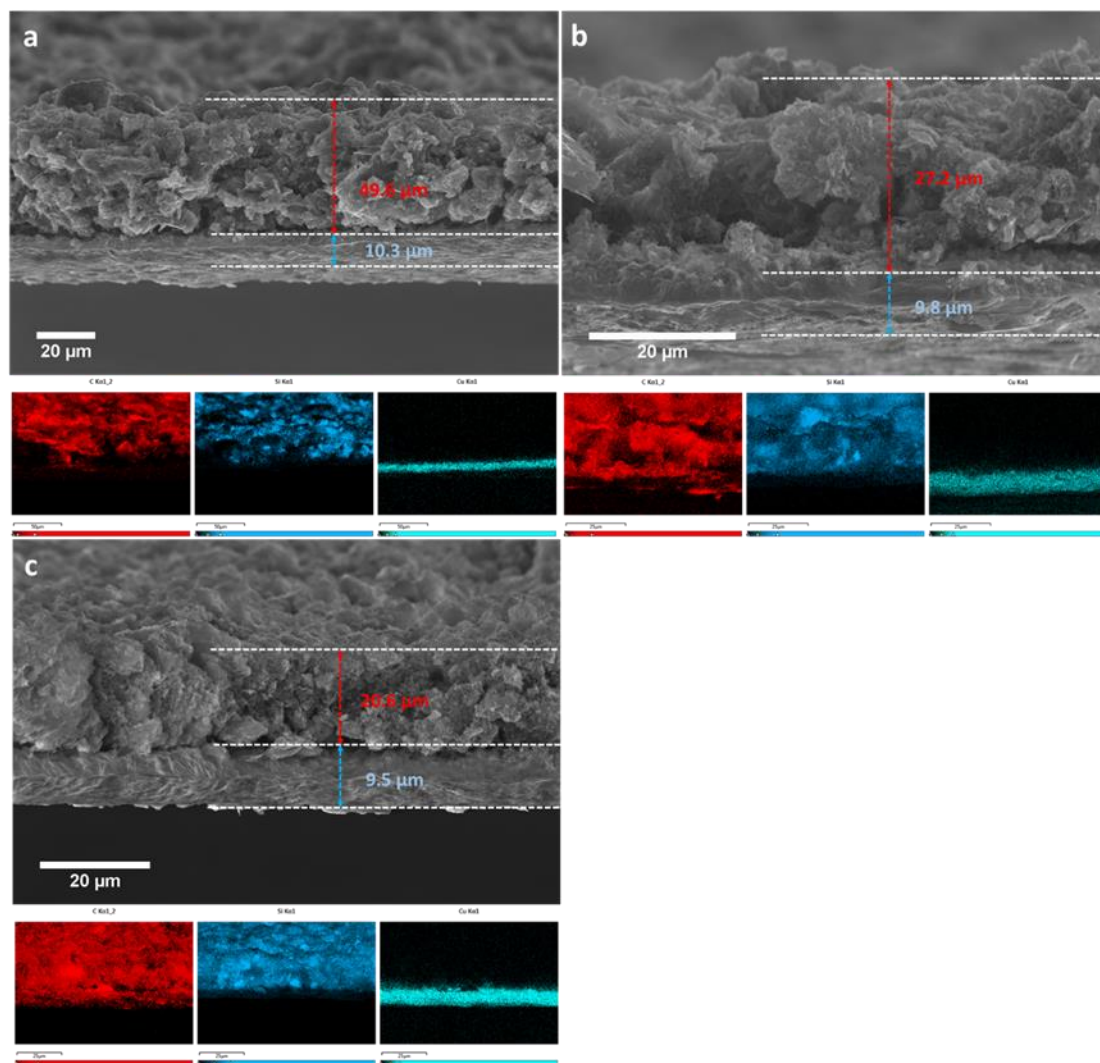


Figure 3.8 SEM of cross section of thick electrode of (a) SGF100/1000/675 with 4.6 mg cm^{-2} areal loading, (b) SGF200/1000/675 with 3.4 mg cm^{-2} areal loading and (c) SGF200/1000/338 with 2.7 mg cm^{-2} areal loading.

Figure 3.9 shows the area capacity, cycle stability and CE under current of 0.5 mA cm^{-2} and 1.0 mA cm^{-2} . The first lithiation-delithiation cycle was carried under 0.1 mA cm^{-2} for formation and activation: the initial capacities of the electrodes of SGF100/1000/675, SGF200/1000/675 and for SGF200/1000/338 are 886 mAh g^{-1} (4.1 mAh cm^{-2}), 1169 mAh g^{-1} (4.0 mAh cm^{-2}) and 1419 mAh g^{-1} (3.8 mAh cm^{-2}), respectively. The ICE was Similar to thin electrodes 59.5%, 77.1% and 70.6%, respectively. And the capacity retention (vs. 2nd cycle) are 81%, 91% and 92%, respectively at current of 0.5 mA cm^{-2} .

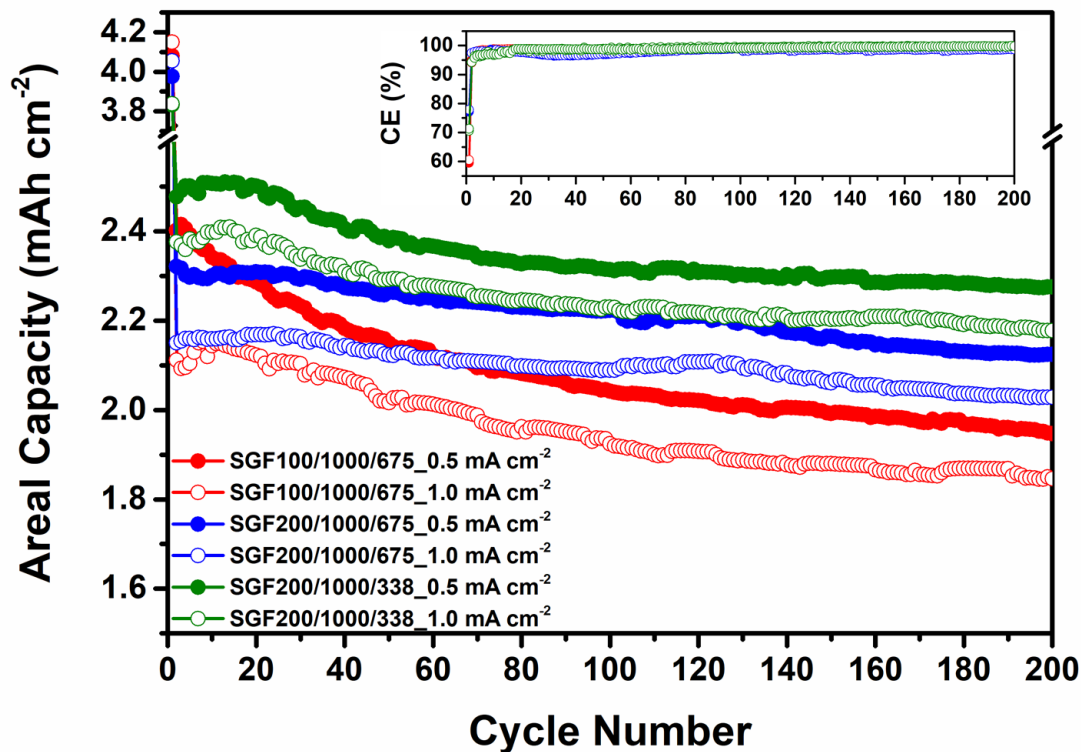


Figure 3.9 cycle stability of thick electrode of Si-GC at current density of 100 mA g⁻¹ with coulombic efficiency as inset.

3.5 Conclusion

In summary, we demonstrated an energy efficiency and scalable production route to synthesize Si-GC composites via magnesiothermic reduction of commercial silica and graphitized carbon coating via low temperature Fe catalytical graphitization. We succeeded

in controlling Si particles size growth and preservation of porous architecture as secondary structure. By incorporating both advantages of graphitic carbon and silicon, with promising electrochemical performance, simple, controllable, low-temperature and low-cost synthesis process, our Si-GC composite is promising for next-generation Li-ion batteries anode.

At beginning of this work, we demonstrated the feasibility of catalytical graphitization.

The XRD shows below demonstrated the formation of graphitic carbon.

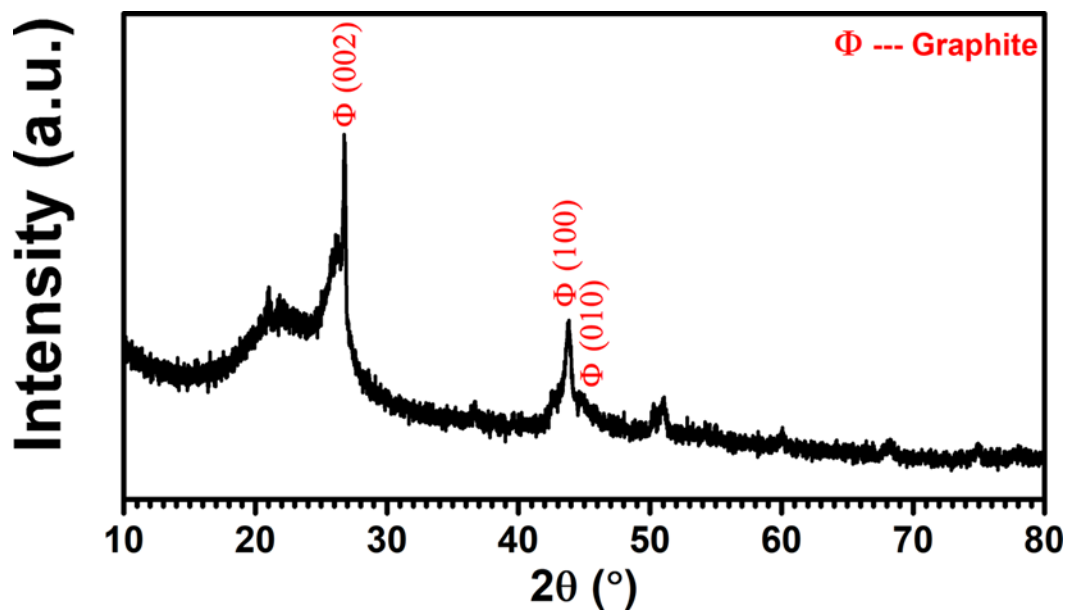


Figure 3.10 XRD of the carbon material derived from glucose with presence of $\text{Fe}(\text{NO}_3)_3$ to promote graphitization.

The TGA characterized the carbon content of graphitic carbon.

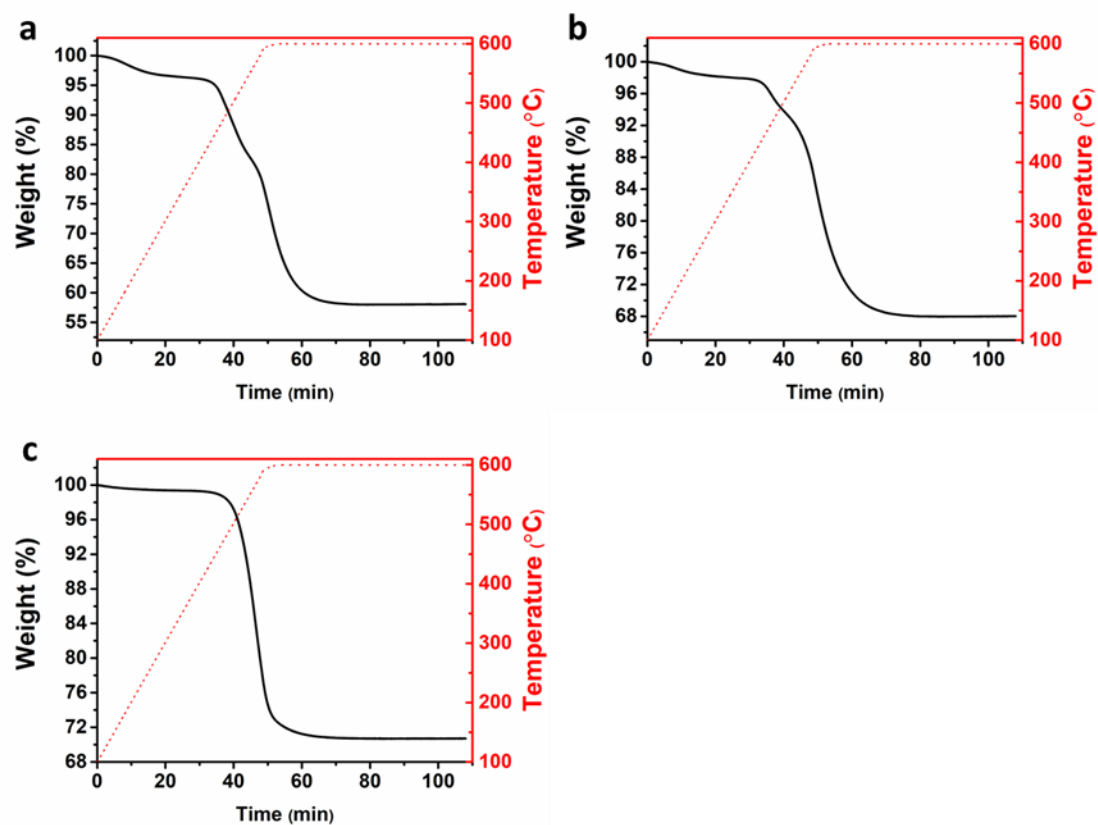


Figure 3.11 TGA curves of Si-GC composite with carbon ratio of (a) SGF100/1000/675 with 42 wt.% carbon, (b) SGF200/1000/675 with 34 wt.% and (c) SGF200/1000/338 with 30 wt.% carbon.

The CV measurement also conducted show in **Figure 3.12**.

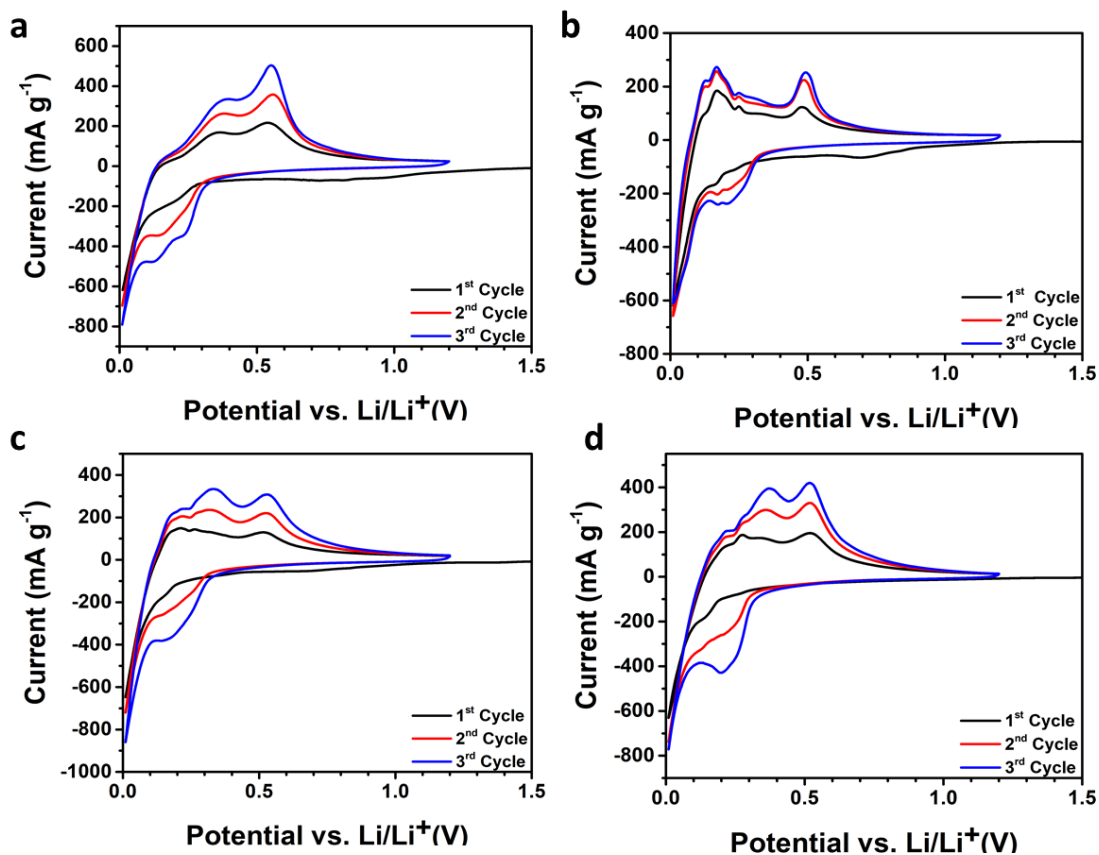


Figure 3.12 representative CV curves of thin electrode of (a) Porous Si; (b) SGF100/1000/675; (c) SGF200/1000/675 and (d) SGF200/1000/338.

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Chapter 4 Summary and Future Directions

4.1 Summary

In chapter 1, started with introducing general background of Li-ion batteries. From working mechanism to methods of performance improvement. Next, we discussed the two-phase transformation mechanism in lithiation and delithiation process and facing challenges like mechanical degradation and unstable SEI. The two major issues hint the commercialization of Si. To have practical applications, strategies of rational design been discussed and summarized the state of the art of Si or Si based composite. Finally, we discussion the magnesiothermic reduction reaction of silica the challenges such as original structure preservation and by-products formation.

In chapter 2, we mainly focused on one of the rational design methods of Si. We delivered a high-performance Si composite anode material using a scalable production route. Aerosol spray drying of the commercial silica water suspension to synthesize porous silica particles as Si precursor. Magnesiothermic reduction reaction and further wash step were proceed. Finally coated a carbon layer via chemical vapor deposition. In addition, we systematically studied the kinetics of magnesiothermic reduction of silica. We optimized the parameters of magnesiothermic reduction reaction and acquired best condition. Subsequently, we demonstrated different carbon coating impacting the electrochemical performance and by

carbon coating can address the low initial coulombic efficiency and enhance the cycle stability. In order to have a practical application, thick electrode was made. The electrode was made of 30% Si-C and 60% Graphite and demonstrate commercialization potential and full cells demonstrated excellent performance as well. In short, magnesiothermic reduction reaction is complicated and uncontrollable, to assure best Si with desired morphology, time, temperature and mixing are critical.

In chapter 3, we conducted other routine to stabilize solid-electrolyte-interphase. As far as we know, solid-electrolyte-interphase is stable. We investigated an energy efficiency and easy scale-up method to synthesize a high-performance graphitized carbon coated silicon composite. Si was produced via magnesiothermic reduction reaction. And graphitic carbon was synthesized via catalytic graphitization which keeping the Si, C system below the critical temperature which promoting the formation of SiC. The Si@GC composite achieved excellent cycle stability, reached and kept specific capacity above 1000 mAh g⁻¹. The thick electrodes demonstrated an excellent performance for 917 mAh g⁻¹ specific capacity and 2.5 mAh cm⁻² areal capacity. Meanwhile, persevered 84% capacity after 200 cycles.

We have successfully developed a facile and controllable method to synthesize porous Si. Meanwhile, comprehensive design for Si anode and obtained the relationship between

product properties and reaction parameters. The kinetics of magnesiothermic reduction of SiO_2 has not been systematically studied to date. The reaction parameters obtained were used in this task to develop the kinetic model to describe the general process of magnesiothermic production of porous Si. Based on the kinetics study, we can obtain the correlation amount temperature, reaction time, particle size and structure to the conversion of SiO_2 . The optimized experimental conditions can be predicated from the model to guide the optimized synthesise.

4.2 Future Directions

Our kinetics study has provided a guidance to choose the right parameters for magnesiothermic reduction reaction. However, this type of reaction rate limitation is controlled by diffusion. The particle size, shape and porosity and whether surface coating has huge impact. On the other hand, magnesiothermic reduction reaction is intensity exothermic reaction. Thus, the amount of reactant and heat scavenger put in the close system reactor do affect the accuracy of the conversion and morphology prediction.

Our current techniques are ready to transfer to manufacturing. With the kinetics model, energy consumption and product yield are easy to estimate the cost. Carbon chemical vapor deposition and low temperature graphitic carbon coating is easy to industrially achieve to enhance the performance of Si. Meanwhile, the relation between amount of reactant and

heat transfer should be modeled to better understand the magnesiothermic reduction reaction.

However, the initial coulombic efficiency has a gap compared to graphite. Our future direction will include, increase the initial coulombic efficiency to or close to graphite. Possible methods including, lower the surface area by more sophisticate carbon or graphitic carbon coating. Meanwhile, change Si structures and particle size may be a good way to increase intimal coulombic efficiency, since through our observation, Si particle with less surface area could alleviate surface reaction, accompanying with more rigid surface carbon coating, makes Si-C composite a promising anode material.