Study of lithium-ion battery anodes based on silicon nanostructures

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NANYANG
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**STUDY OF LITHIUM-ION BATTERY ANODES
BASED ON SILICON NANOSTRUCTURES**

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**SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

2014

STUDY OF LITHIUM-ION BATTERY ANODES BASED ON SILICON NANOSTRUCTURES

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Abstract

Silicon is well known as a very promising anode material because it has an extremely high theoretical specific capacity of $\sim 4200 \text{ mA h g}^{-1}$ and some other advantages such as low discharge potential, non-toxicity and abundance, etc. However, it is found that anodes based on bulk or micron-sized Si exhibit very poor cycling performance due to the structural pulverization caused by significant volume changes (upto 400%) of Si during Li^+ insertion/extraction processes. On the other hand, nanostructured Si has been shown to alleviate this problem because it has a large portion of surface atoms that could effectively release internal strain through the surrounding space. This dissertation focuses on the design and fabrication of lithium ion battery anodes based on Si nanostructures and the investigation of their charge/discharge behaviors.

The first nanostructure demonstrated in this PhD project is a Si-Ni cone array comprised of supportive Ni particles rooted on a Cu foil current collector and electrochemically active Si coatings. In this structure, each Ni particle and its Si coating form a unique vertical cone rooted on the current collector. With the spherical Ni particle support, the Si coating is able to expand/contract along radial direction of Ni cores to release its internal stress through out-of-plane directions, instead of accumulating a large in-plane stress. Scanning electron microscopy images show that the cone array still adheres to the substrate after cycling and some cracks have developed along boundaries of the cones to help

release internal stress, while the Si cones show no crack or pulverization. As a result, the composite anode shows quite good capacity retention and rate performance, significantly better than a conventional Si thin film anode with the same amount of amorphous Si loading.

The second nanostructure demonstrated is carbon nanotube (CNT)-Si core-shell wire arrays rooted on a stainless steel current collector. The structure employs vertically aligned CNTs with controllable diameters and spacing as the core. Anodes based on the CNT-Si wire arrays with large core nanowire diameters and large inter-wire spacing demonstrate excellent electrochemical performance that is superior to most core-shell Si nanowires (SiNWs) previously reported. The good performance can be mainly attributed to two factors. First, small curvature of the thick CNT core effectively reduces the detrimental hoop stress in the Si shell. Second, the vertical alignment and large inter-wire spacing of the nanowire array provide sufficient space to accommodate radial volume change of the Si shell and promote access of electrolyte to the whole structure. The electrode shows well maintained morphology and almost intact core-shell structures after repetitive cycling, further confirming the advantages of the fabricated structure in effective strain relaxation. The CNT-Si core-shell structure is further improved by engineering the morphology of the Si shell such that its thickness gradually decreases along the CNT core from top to bottom of the array. The gradient Si shell eliminates structural damage caused by volume change of Si coating on current collector

surface and at CNT roots. As a result, the capacity retention of the CNT-Si anode is further improved.

During my PhD study, a novel method to fabricate SiNW arrays has also been developed. In this method, a monolayer of well-spaced metal particles is synthesized on Si substrate through a simple *in situ* dewetting process. With the metal particles as a sacrificial template, a large area catalyst metal mesh is then fabricated. Finally, SiNW arrays are obtained by performing solution etching with the metal mesh as the catalyst. Compared to previously reported methods to fabricate SiNW arrays with controllable diameters and spacing, our method is more repeatable, scalable and easier to control. The method is expected to be promising for many practical applications such as lithium ion batteries and solar cells.

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List of Abbreviations

LIB: lithium ion battery

CNT: carbon nanotube

SiNW: Si nanowires

EV: electric vehicle

HEV: hybrid electric vehicle

SS: stainless steel

SEI: Solid electrolyte interphase

EC: ethylene carbonate

DEC: diethyl carbonate

CV: cyclic voltammetry (voltammogram)

TEM: transmission electron microscopy

XRD: X-ray diffraction

PVDF: polyvinylidene fluoride

NMP: *N*-methyl-2-pyrrolidone

SBR: styrene butadiene rubber

CMC: sodium carboxymethylcellulose

PAA: polyacrylate

PVD: physical vapor deposition

CVD: chemical vapor deposition

AAM: anodized alumina membrane

ROCO₂Li: alkyl Li carbonates

EMC: ethylmethyl carbonate

FEC: fluoroethylene carbonate

VC: vinylene carbonate

IPA: isopropyl alcohol

EDX: energy-dispersive X-ray spectroscopy

SEM: scanning electron microscope

PC: propylene carbonate

CNF: carbon nanofiber

PECVD: plasma enhanced chemical vapor deposition

PV: photovoltaic

VLS: vapor liquid solid

RIE: reactive ion etching

MACE: metal assisted chemical etching

EBL: electron beam lithography

IL: interference lithography

PS: polystyrene

Chapter 1

Introduction

1.1 Motivation

Over the past centuries, people have been relying on burning fossil fuels to generate energy for both industrial and personal uses. Fast depletion of world oil resources and increasingly severe environmental crises such as air pollution and climate warming caused by the traditional fossil fuel energy resources are forcing people to explore alternative energy resources that are cheap, clean and sustainable. Solar, wind and waves are very good alternatives to which much effort has been dedicated in the past decades. However, these new energy resources also need high efficiency storage devices to store extra energy generated and release it when necessary. Rechargeable battery is a good choice because it can reversibly convert electrical energy into electrochemical energy stored and release it when necessary. Of the several available rechargeable battery systems, the lithium ion battery (LIB) exhibits the highest energy density, output voltage and power performance, as summarized in Fig. 1.1. Since its commercialization by SONY in 1991, LIB has quickly conquered the whole portable electronics market and is also considered the most promising energy storage device to power future electric vehicles (EVs) and hybrid electric vehicles (HEVs) with zero or low carbon dioxide emission. Fig. 1.2

shows statistics and projection of LIB sales in the consumer electronic and HEV market.

Fig. 1.1 Comparison of different battery technologies in terms of volumetric and gravimetric energy density. Li-ion and plastic lithium-ion (PLiON) batteries are superior in energy density to traditional lead-acid, nickel-cadmium (Ni-Cd) and nickel-metal hydride (Ni-MH) batteries. PLiON is different from traditional LIBs in a way that its electrolyte contains a polymer matrix swollen with liquid solvent and lithium salts, offering shape flexibility.¹

Fig. 1.2 Evolution and projection of LIBs in the consumer electronic and HEV markets.²

Despite the impressive growth in worldwide sales, LIB technology has been criticized for its sluggish advancement that eventually slows down the deployment of powerful electronics and electric cars. There are many factors that could affect a battery's overall performance, e.g. electrode materials, electrolytes and packages. However, electrode materials are regarded as a dominating factor as their electrochemical properties determine the maximum amount of energy that can be stored in a battery. Therefore, the key to develop advanced batteries is to explore high capacity materials for both anodes and cathodes. Commercial LIBs employ carbonaceous materials such as graphite as the anode. To further improve the capacity of a battery, advanced materials with higher capacities are desired. Silicon is a promising candidate because study of the Li-Si binary system suggests that upon full lithiation, each Si atom can accommodate 4.4 lithium atoms, leading to a high specific capacity of 4200mA h g⁻¹,³ which is more than 10 times higher than that of commercial graphite anode (372mA h g⁻¹) and is the highest among all available materials. In addition, Si is abundant, non-toxic and easy to prepare, making it an ideal anode material for large-scale commercial applications.

Unfortunately, the extremely high Li⁺ intake capability also results in a significant volume change during charge/discharge. The formation of Li_{4.4}Si is accompanied by a volume expansion of ~400% and the volume is restored during subsequent de-lithiation process.³ Consequently, electrodes based on bulk or micrometer sized Si always show very poor capacity retention due to volume change induced pulverization that causes loss of electrical contact

between active materials and current collectors.⁴ Later, it was found that the pulverization problem could be significantly alleviated by employing nanostructured Si that is more resistant to volume change induced stresses than its bulk counterparts. Moreover, nanostructures also offer some other advantages such as short charge transport length to enable high rate performance, which is crucial for EV or HEV applications.

1.2 Objectives

The objectives of my PhD project are:

- To design and fabricate advanced Si nanostructures for LIB anodes
- To study electrochemical behaviors of the synthesized Si nanostructures
- To investigate structural evolution of the Si nanostructures during electrochemical cycling
- To investigate fading mechanism of the LIB anodes based on Si nanostructures for further improvements

1.3 Major contributions of this thesis

The major contributions of my PhD study are as follows:

- Arrays of Si-Ni cones, each consisting of a cone shaped Si shell supported by a Ni particle core rooted on a Cu foil current collector, are fabricated and utilized as LIB anodes. The Ni particles are synthesized by

annealing a Ni thin film on TiN coated copper foil. The Si cones are realized using RF magnetron sputtering with the Ni particles as nucleation centers. The Si-Ni cone array anode shows much better capacity retention than a Si thin film anode with the same Si mass loading. The good performance is attributed to the spherical contact interface between the Si coating and Ni support that enables radial expansion/contraction of Si shell during charge/discharge to favor volume change in out-of-plane directions and suppress detrimental in-plane expansion/contraction. Post-cycling electrode surface morphology characterization indicates that stress induced by big volume change is released through initiation and propagation of cracks along the cone boundaries, while the Si cones show no crack or pulverization, indicating a good structural stability of the Si coating.

➤ Vertically aligned carbon nanotubes (CNTs) with large diameters and large inter-wire spacing are fabricated directly on stainless steel current collectors and investigated as the core for core-shell Si nanowires (SiNWs). Compared to previously reported core-shell SiNWs, the large core diameters and large inter-wire spacing in our CNT-Si structure effectively reduce hoop stress in the Si shell and provide sufficient space to more effectively accommodate volume change of the Si shell during charge/discharge. As a result, the CNT-Si anode demonstrates excellent electrochemical performance that is superior to most core-shell SiNWs anodes previously reported. To further confirm the benefits of employing the thick CNT core, a control sample with thin CNT cores is also demonstrated with inferior electrochemical

performance. Structural characterization of the CNT-Si core-shell nanowires anode after cycling indicates that excessive strain accumulation at the wire roots is a main cause of capacity fading after long-term cycling. The strain originates from volume change of the Si at CNT roots and on current collector surface. To handle this problem, the morphology of the Si shell is further engineered such that its thickness gradually shrinks along the CNT core from top to bottom of the array. The gradient Si shell eliminates the excessive strain at the wire roots and leads to long-term structural stability of the CNT-Si anode. As a result, cycling performance of the CNT-Si anode is further improved.

➤ A simple, reliable and scalable method is developed to fabricate vertically aligned SiNWs at low costs. A monolayer of well-spaced dewetted metal particles on Si substrate is used as a sacrificial template to obtain a catalyst Au mesh. SiNWs are then obtained by etching the Si substrate in an etching solution with the Au mesh as the catalyst. Compared to previously reported techniques, our method is more repeatable, scalable and easier to control. The method is expected to be very promising in practical applications of SiNW arrays.

1.4 Organization of this thesis

This thesis is organized as follows:

In Chapter 1, the motivations and objectives of this PhD study as well as the major contributions are introduced.

Chapter 2 gives a brief introduction of LIB technology, including its development history, components and basic working mechanism to help readers gain fundamental knowledge of this technology. Two techniques, i.e., cyclic voltammetry and galvanostatic charge/discharge that are employed to characterize electrochemical performance of LIB electrodes in this PhD study are also briefly discussed. This chapter also provides a detailed review of lithiation/de-lithiation mechanisms, typical charge/discharge behaviors, major problems and research status of Si anodes because this PhD study focuses on Si anodes.

Chapter 3 is dedicated to the Si-Ni cone arrays, which is the first Si anode demonstrated during my PhD study. The experimental design, fabrication processes, structural and electrochemical characterizations, and experimental results are addressed in detail.

In Chapter 4, Si anodes based on CNT-Si core-shell wire arrays directly rooted on a SS current collector is introduced. The improvements of this structure over previous core-shell nanowires are well addressed. Electrochemical performance,

including cyclic voltammogram, cycling performance and rate performance is systematically investigated and related to structural characteristics of this structure.

Chapter 5 presents an advanced CNT-Si core-shell anode in which the Si shell is engineered with a gradient morphology. The originality and fabrication process of this unique structure are introduced, followed by structural/electrochemical results and discussion.

In Chapter 6, a novel method to fabricate SiNW arrays with controllable diameters and spacing is presented. The detailed fabrication process and the advantages/limitations of this method over existing methods are addressed in detail.

Chapter 7 summarizes the achievements of this PhD project and gives recommendations for future work based on the findings of my PhD study.

Chapter 2

Lithium ion battery

2.1 Development history

Early lithium rechargeable batteries employ lithium metal as the anode. The motivation for using lithium as the anode is inspired by the fact that Li is the most electropositive (-3.04 V versus standard hydrogen electrode) as well as the lightest metal (equivalent weight $M = 6.94$ g/mol, and specific gravity $r = 0.53$ g/cm³), thus facilitating the realization of high energy density energy storage systems.¹ This was firstly demonstrated in the 1970s in a primary Li cell. With the high energy density and variable discharge rates, Li cells rapidly found applications in watches, calculators and medical devices. Over the same period, many inorganic compounds such as TiS_2 were found to react with Li^+ in a reversible way and triggered the development of Li rechargeable batteries employing Li metal as the anode and an intercalation compound as the cathode. However, Li rechargeable batteries were soon found to be unviable because of the dendrite problem at the Li metal/liquid electrolyte interface. To put it more clearly, on discharge, Li atoms in the Li metal anode are oxidized to Li ions

which are driven by an internal electrical field to pass through the electrolyte to react with cathode. On charge, an opposite potential applied to the battery forces Li ions to leave the cathode and pass through the electrolyte to the Li metal anode where they are reduced to Li and deposit to the Li metal anode. However, the Li ion do not simply deposit to their original locations but tend to form dendrites at Li metal/electrolyte interface, as schematically illustrated in Fig. 2.1. After many cycles, the continuously growing dendrites may penetrate the electrolyte and short the cathode, causing a sudden increase in temperature or even explosion.

Fig. 2.1 Schematic illustrate of dendrites in lithium metal batteries.¹

To circumvent this problem, one approach was to replace Li metal anode with another insertion material, giving rise to the “rocking chair” lithium ion battery, as demonstrated by Murphy *et al.* at the end of the 1980s.⁵ Meanwhile, to compensate for the increase in potential of the anode, higher potential cathode materials were used to replace the transition metal disulphides.

Finally, discovery of the highly reversible Li^+ intercalation-deintercalation process in carbonaceous material led to the commercialization of C/LiCoO₂ LIBs by SONY in 1991.¹

2.2 Components and working mechanism

A battery is composed of several electrochemical cells that are connected in series and/or in parallel to provide the desired voltage and capacity. Each cell consists of three basic components---anode, cathode and electrolyte. The anode and cathode are used to store energy on charge and release the stored energy on discharge. The electrochemical potential difference between the anode and cathode determines open circuit voltage of the battery. Normally, cathode materials with relatively high electrochemical potentials and anode materials with relatively low potentials are preferred to maximize output voltage of the battery. However, the electrochemical potential has to be within the stability potential range of the electrolyte to prevent reactions of electrodes with electrolyte, which will be addressed in more detail later. The electrolyte is a mixture of several organic solvents containing dissociated lithium salts that enables Li^+ transport between the two electrodes. A good electrolyte should have a high ionic conductivity to facilitate fast Li^+ transport between the two electrodes and a low electronic conductivity to minimize self-discharge of batteries. Besides, there are some other complementary components, e.g. current collectors attached to both electrodes, a separator that physically

separates anode and cathode. For commercial LIBs, the current collector for anode is a thin Cu foil because Cu is inert at low working potentials (vs. Li/Li^+) of anodes. For cathodes, the current collector is a thin Al foil due to its stability at high working potentials. The separator is usually a porous fibrous membrane.

LIBs have to be charged first before use. Take the commercial C/LiCoO₂ system as an example, on battery charge, a voltage larger than the output voltage of the battery is applied in opposite polarity to the two electrodes. Electrons in the LiCoO₂ cathode will be forced to flow through the external circuit to the carbon anode. Meanwhile, Li^+ in the cathode will migrate through the electrolyte to the anode. As a result, the carbon anode is reduced to Li_xC and the LiCoO₂ cathode is oxidized to $\text{Li}_{1-x}\text{CoO}_2$, thus the external electrical energy is transformed to chemical energy and stored in the battery. On battery discharge, an electric load is connected to the electrodes. As the cathode has a higher potential than the anode, electrons in Li_xC anode spontaneously flow to $\text{Li}_{1-x}\text{CoO}_2$ cathode through the external circuit and deliver electrical energy to the load. Meanwhile, Li ions previously intercalated in the anode flow through the ionic conductive electrolyte to the cathode to maintain charge balance. After battery discharge, the Li_xC anode is oxidized to C and the $\text{Li}_{1-x}\text{CoO}_2$ cathode is reduced to LiCoO₂, as schematically illustrated in Fig. 2.2.

Fig. 2.2 Schematic illustrating working mechanism of a LIB during charge and discharge.⁶

2.3 Solid electrolyte interphase (SEI)

Generally, SEI is formed by side reactions between electrode and electrolyte at their interface during the first Li^+ intercalation process. Electrolyte is lithium salt containing liquid that provides ionic conduction between anode and cathode. The solvent used is usually a mixture of several carbonates with different physical and chemical properties to meet diverse requirements of ionic conductivity, viscosity, etc. Each solvent is thermodynamically stable within a certain potential range. Beyond the range, the electrolyte will be oxidized by the highly oxidative cathode and below the range the electrolyte will be reduced by the highly reductive anode. For example, a common electrolyte system currently used is 1M LiPF_6 dissolved in ethylene carbonate (EC)/diethyl

carbonate (DEC) (1:1). Fig. 2.3 shows operating potentials of several common electrode materials relative to the window of this electrolyte system.

Fig. 2.3 Voltage versus capacity of several electrode materials relative to the window of the electrolyte 1M LiPF₆ in EC/DEC (1:1).⁷

From the figure, operating potentials of several materials, such as graphite, are outside the stability window of the electrolyte. So thermodynamically, the electrolyte is not stable when in contact with graphite and will react with it, leading to the formation of a solid-electrolyte-interphase (SEI) film consisting of several reaction products at the surface of graphite. Generally, composition and stability of the SEI film are dependent on both electrode material and electrolyte composition. The benefit of SEI is that its formation virtually enlarges the operating potential range of the electrolyte to allow for operation of some reactive electrode materials with kinetics stability, e.g. graphite. Unfortunately, in most cases, an unstable SEI is usually generated

and it continuously consumes electrolyte and contributes to capacity fading of the battery. Such a problem can be alleviated by electrode surface passivation coating or modification of electrolyte compositions to generate a stable SEI, which will be discussed in more detail later.

2.4 Electrochemical characterization

Electrochemical characteristics of LIB anodes or cathodes are usually tested by assembling the electrode into a half-cell with lithium metal foil as the counter electrode. A detailed assembly process is described in Section 3.2 of this thesis. Cyclic voltammetry (CV) and galvanostatic charge/discharge are the two most common techniques.

CV is an electro-analytical technique to study redox systems. During a typical process, the potential between working and reference electrodes is ramped linearly versus time at a user-defined scan rate. When the set potential is reached, the potential ramping polarity is reversed. Such reversion could happen multiple times in a predefined potential range. Meanwhile, the current in the working electrode is measured and plotted against the applied potential to generate a cyclic voltammogram (CV). A CV test could be used to determine oxidation and reduction potentials of a redox system in a potential range. The measured current increases fast when an oxidation (or reduction) potential is reached due to oxidation (or reduction) reaction induced charge transfer and decays fast when reaction species at electrode/electrolyte interface are depleted.

For LIB half-cells, the oxidation/reduction potentials correspond to lithiation/de-lithiation potentials of the working electrode.

Galvanostatic charge/discharge is used to determine charge/discharge voltage profiles and capacities of battery electrodes. In a typical process, a constant current is either withdrawn from (for lithiation process) or fed into (for de-lithiation process) the working electrode until its potential reaches the upper or lower cut-off. Discharge/charge capacities of the electrode can be calculated according to the formula $C=I \times t$ (in mA h) where I is the charge/discharge current, t is charge/discharge duration. The capacity C is then normalized by the active material mass in the electrode or the electrode area to obtain the gravimetric specific capacity (in mA h g⁻¹) or the areal specific capacity (in mA h cm⁻²). For anodes such as graphite and Si that contain no Li⁺, a lithiation process is carried out first to alloy the anode before it can be de-lithiated. On the contrary, cathodes such as LiCoO₂ and LiMn₂O₄ are usually de-lithiated first. A capacity vs. voltage (C-V) curve is obtained by plotting the potential of working electrode against capacity (or time) during charge/discharge processes. For example, Fig. 2.4 shows the first cycle voltage profiles (C-V curve) of a Si anode over the potential range of 0.01-1.2 V.

Fig. 2.4 Charge/discharge voltage profiles of a Si anode.

Galvanostatic charge/discharge is usually repeated for a few cycles to assess cycling performance of an electrode. In addition, the rate performance of an electrode could also be determined by varying charge/discharge currents.

2.5 Advanced electrode materials

Since the commercialization of LIBs, most production today still relies on C/LiCoO₂ electrodes. However, to meet the requirements of future powerful consumer electronics and electric vehicles, advanced high capacity materials for both anode and cathode are in great demand. For cathode materials, current LiCoO₂ has two major limitations. First, theoretical capacity of LiCoO₂ is 274 mA h g⁻¹ if all of Li ions can be extracted. But practically only around half of Li

ions are used to maintain structural stability of LiCoO_2 , giving rise to a practical capacity of around 179 mA h g^{-1} , which is substantially lower than that of graphite anodes. Second, the low natural reserve of cobalt makes LiCoO_2 rather expensive. The material is also toxic and therefore not a good choice for large scale production. Current research on cathode mainly focuses on two systems, LiMn_2O_4 and LiFePO_4 . Compared to LiCoO_2 , although the two candidates are not superior in terms of the theoretical capacity, they are much cheaper and non-toxic and partial commercialization has been realized. In contrast, the progress of anode materials is rather slow compared to that of cathode materials. This is mainly attributed to the good properties of carbonaceous anodes (e.g. low-cost, non-toxic and good overall electrochemical performance). Therefore, it is quite difficult to find a suitable substitute to replace carbon. A major concern with graphite is the potential lithium plating hazard associated with its very low intercalation potential ($\sim 0.05 \text{ V}$ versus Li/Li^+). Therefore, current research efforts focus on searching for materials with a slightly higher lithiation potential and higher theoretical capacity. In this regard, there are several promising candidates, e.g. oxides, nitrides and metals. Among the candidates, alloy electrodes have attracted special attention owing to their extremely high specific capacities and slightly higher lithiation potentials.

In the early 1970s, several groups demonstrated that a number of metallic or semi-metallic elements could be electrochemically alloyed with lithium at room temperature.^{8 9} Up to now, many metals have been found to be electrochemically active towards lithium, e.g., Si, Sn, Al, Sb, Mg, Bi, In, Zn, Pb,

Ag, Pt, Au, Cd, As, Ga and Ge. However, only the first five metals are intensively investigated because of their abundance and non-toxicity that make them attractive and appealing for practical applications.¹⁰ In contrast to graphite anodes where every six carbon atoms accommodate one Li^+ upon full lithiation, each atom in an alloy anode can accommodate more than one Li^+ , leading to substantially higher capacities. Fig. 2.5 below compares gravimetric and volumetric capacities for some selected alloy electrodes in comparison with that of graphite.

Fig. 2.5 Gravimetric and volumetric capacities of several alloying materials.¹¹

It is remarkable that many materials have much higher capacities than graphite, e.g. Sn, Al and Si. Actually, the first commercial cell introduced in the 1980s was based on a metal alloy of Bi, Pb, Sn and Cd. When the dendrite problem of employing lithium metal anode was identified, Al alloy anode was also demonstrated with higher safety.¹ However, alloy anodes did not succeed because they had very poor capacity retention, especially when subjected to

deep discharge. The main problem resulted from their huge volume change upon lithium insertion/extraction, which could be as large as 400%. In graphite anodes, Li^+ reversibly intercalate/de-intercalate from the space between adjacent graphene layers, leading to only 10% change in graphite volume. In contrast, each atom in a dense alloy anode has to accommodate more than one Li^+ , resulting in significant volume changes during lithiation/de-lithiation cycles. Consequently, alloy electrodes easily get pulverized after only several cycles and a fast capacity fade is observed. In recent years, demand for high energy density LIBs urged people to re-examine the viability of high capacity alloy anodes and a lot of efforts are being dedicated to alleviating the volume change problem. Fig. 2.5 also indicates that among the alloy materials, Si exhibits the highest theoretical specific capacity which is substantially higher than the other materials, making it a very popular research subject. In the next part of this chapter, Si and its properties as an anode material for LIBs will be addressed in detail.

2.6 Si anodes

2.6.1 Electrochemical characteristics

Si is a very promising material for future LIB anodes owing to several attributes. First, Si has a very high theoretical specific capacity. In its fully lithiated composition, $\text{Li}_{22}\text{Si}_5$, Si shows an extremely high theoretical specific capacity of 4200 mA h g^{-1} , compared with 3600 mA h g^{-1} for lithium metal and

372 mA h g⁻¹ for graphite. The specific capacity of Si is the highest among all materials including elements and compounds. Second, Si exhibits an onset potential of 0.3~0.4 V versus Li/Li⁺, minimizing any risks of Li plating as with graphite anodes (~0.05V vs Li/Li⁺) without compromising output potential of LIBs.¹⁰ In addition, Si is the second most abundant element on earth, which translates to a low material cost. Besides, Si is non-toxic, eliminating any environmental concerns.

Charging/discharging behaviors of Si anodes vary with several factors. The lithium alloying process of Si at 415°C leads to sequential formation of several binary phases Li₁₂Si₇, Li₁₄Si₆, Li₁₃Si₄ and Li₂₂Si₅, with onset potentials of 332, 288, 158, and 44 mV, respectively.³ At room temperature, although several papers claimed to observe the formation of the crystalline Li₂₂Si₅,^{12 13} most investigations only achieved the highest lithiated phase of Li₁₅Si₄, corresponding to a specific capacity of 3579 mA h g⁻¹.^{14 15} Also, the alloying process at room temperature follows a different scheme and the voltage profiles are affected by Si morphology and lithiation depth etc. Fig. 2.6 presents voltage profiles of Si anodes based on crystalline Si particles of several microns.¹⁴ During the first lithiation process, a long and flat plateau at ~0.1 V was displayed, indicating a two-phase reaction. The following lithiation curves showed no distinct plateau, indicating single phase reactions. Meanwhile, the de-lithiation curve shapes were dependent on lithiation cut-off potential. If the anode was lithiated to 0 V, a plateau at ~0.4 V was shown in the lithiation curves (Fig. 2.6a). However, if the cut-off was restricted to above 50 mV, the

de-lithiation curves showed no distinct plateau. As demonstrated in Fig. 2.6b, the lithiation cut-off potential for the first two cycles was 50 mV, subsequent de-lithiation curves showed a distinct plateau at ~ 0.4 V. For the following cycles, the cut-off was 70 mV and no plateau was observed in the de-lithiation curves.

Fig. 2.6 Charge/discharge voltage profiles of Si particles (a) with a lithiation cutoff of 0 V and (b) with a lithiation cutoff of 50 mV for the first two cycles and 70 mV for later cycles.¹⁴

Structural changes in the crystalline Si powder anodes were investigated by X-ray diffraction (XRD) studies.¹⁴ It was found that during the first lithiation process, the crystalline Si particles were gradually transformed to an amorphous Li_xSi phase which co-existed with crystalline Si to form a two-phase reaction at above 50 mV. Fig. 2.7 shows a high resolution transmission electron microscopy (TEM) image of the phase boundary between crystalline Si and

amorphous Li_xSi during lithiation.¹⁶ The two-phase reaction resulted in a flat plateau at ~ 0.1 V in the first lithiation curve. Below 50 mV, the amorphous phase suddenly crystallized to $\text{Li}_{15}\text{Si}_4$. The subsequent de-lithiation caused the crystalline $\text{Li}_{15}\text{Si}_4$ to amorphize and therefore a characteristic plateau at ~ 0.4 V was shown, because of the co-existence of crystalline $\text{Li}_{15}\text{Si}_4$ and amorphous Li_ySi . As the de-lithiation proceeded, the amorphous Li_ySi was gradually transformed to amorphous Si and therefore the de-lithiation curve showed a sloping behavior. When the lithiation cut-off was limited to above 50 mV to avoid the formation of the crystalline $\text{Li}_{15}\text{Si}_4$, subsequent de-lithiation was a solid-solution reaction from amorphous Li_zSi to amorphous Si, resulting in a sloping curve.

Fig. 2.7 TEM image of the phase boundary between crystalline Si and amorphous Li_xSi .¹⁶

The voltage profiles of Si anodes are also affected by sizes of the Si particles. For Si particles of 50-200 nm, their de-lithiation voltage profiles showed no distinct plateau, even if they were lithiated to 0 V, as shown in Fig. 2.8.¹⁷

Fig. 2.8 Charge/discharge voltage profiles of nano-sized Si particles.¹⁷

For amorphous Si thin film anodes, the charge/discharge behaviors were found to be affected by the film thickness and surface roughness, etc. XRD studies concluded that the crystalline $\text{Li}_{15}\text{Si}_4$ phase only formed when the film thickness was larger than $\sim 2 \mu\text{m}$. Generally, thicker Si films exhibited flat delithiation curves, while thinner Si films exhibited sloping curves, as shown in Fig. 2.9.¹⁵ In addition, the formation of the crystalline $\text{Li}_{15}\text{Si}_4$ was found to be suppressed on a rough substrate surface.¹⁸

Fig. 2.9 Charge/discharge profiles of Si films with different thickness.¹⁵

2.6.2 Rate performance

In addition to a high theoretical capacity, a good charge/discharge rate is another requirement to advanced LIB electrodes. This characteristic is especially important for LIBs in hybrid electric vehicles applications. For a LIB electrode, its charge/discharge rate is mainly determined by two factors, Li^+ diffusion coefficient and electrical conductivity. The diffusion coefficient of Li^+ in Si has been investigated by several groups. Ding *et al.* studied diffusion coefficients of Li^+ in nano-Si using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT).¹⁹ They determined the diffusion coefficient to be $\sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Although this value is about one magnitude lower than that in graphite,²⁰ rate performance of Si anodes is actually constrained by the low electrical conductivity, which has been demonstrated by many works. For instance, Ozin's group demonstrated a LIB anode based-on a Si inverse-opal structure fabricated by CVD into the interstices of silica opal templates and subsequent removal of the template. The structure showed high capacities at low currents but decent capacity retentions due to its low electrical conductivity. With a simple heat treatment to enhance its electrical conductivity, the Si inverse-opal structure achieved significantly improved rate performance.²¹ Liu *et al.* fabricated an electrochemical device with a single SiNW as the anode and carried out a real-time observation of lithiation/de-lithiation of the SiNW. They demonstrated that with a same potential applied between the cathode and anode, the lithiation/de-lithiation speed is 1-2 orders of magnitude faster in P-doped or

carbon-coated SiNWs, compared to intrinsic SiNWs.²² Meanwhile, a few of *ex situ* experiments have also demonstrated the benefits of metallic coating in enhancing electrical conductivity and improving rate performance of Si anode.^{23, 24}

2.6.3 Challenges and strategies

Despite possessing a very promising theoretical charge/discharge capacity, Si anodes based on bulk or micron sized Si show very poor cycling performance. Fig. 2.10 shows charge/discharge voltage profiles of a Si anode based on micro-meter sized Si powders. The Si anode exhibited a very high first cycle irreversibility of 35% and a fast capacity fading behavior. The poor cycling performance is mainly caused by the huge volume change of Si during lithiation/de-lithiation cycles. At room temperature, upon the formation of the fully lithiated $\text{Li}_{15}\text{Si}_4$, silicon's volume would expand by ~300%, giving rise to a large compressive stress.²⁵ Upon complete de-lithiation, Si almost restores to its initial volume, the significant volume contraction leads to a large tensile stress in Si that eventually causes cracking and pulverization of Si. As a result, more and more Si pulverizes and loses electronic contact with the current collector as the electrode cycles. A fast capacity fading as shown in Fig. 2.10 was therefore observed.

Fig. 2.10 Charge-discharge voltage profiles of a Si anode based on 10 μm Si powders.²⁶

To maintain structural stability of Si electrodes and achieve good capacity retention for practical lithium-ion battery (LIB) applications, the significant volume change problem must be properly tackled. For traditional powder based electrodes, strategies focus on either engineering Si particles to form multiphase composites or employing elastomer binders. In addition, Si thin films have also attracted intensive research attention owing to their good performance. In recent years, nanostructuring emerges as a very popular research topic because of the advantages of nanostructures in strain accommodation.

2.6.3.1 Si powder anodes

Traditional LIB electrode materials are in powder forms. Electrodes are fabricated by mixing and casting materials in which the active materials are first mixed with a small amount (5-15 wt.%) of conductive additives (e.g. carbon black powders) and polymer binders (e.g. polyvinylidene fluoride (PVDF)) and dissolved in a liquid solvent (e.g. *N*-methyl-2-pyrrolidone (NMP)). After thoroughly mixing to form homogeneous viscous slurry, the mixture is then coated onto the current collectors, annealed to evaporate the solvent and mechanically pressed to enhance the contact with the current collector and within the film. In the final coated film, the polymer binder forms a continuous network that works as a frame to embed the active materials. The conductive powders are uniformly dispersed in the coated film to enhance overall electrode conductivity. This technique works well for materials such as graphite and LiCoO_2 whose volume does not change much upon charge/discharge. But for alloy electrodes such as Si, the significant volume change would destroy the integrity of the overall electrode and cause some materials to get isolated and lose electrical contact with the current collector. Therefore a very fast capacity fading is observed.

Early strategies to tackle the huge volume change problem focused on either engineering the Si particles to form multiphase composites in which Si was dispersed in an active/inactive matrix or replacing traditional PVDF binder with more elastomer polymers to form more flexible networks.

(a) Inactive matrix

For this type of composites, the matrix material is electrochemically inert against Li^+ during lithiation/de-lithiation processes and works as a buffer to accommodate the volume change of Si and prevent pulverization of the anode. To serve this purpose, the inactive matrix must exhibit high mechanical strength to withstand the huge volume expansion of Si. In addition, high electronic conductivity is also required to facilitate fast charge transfer. The matrix could be a metal such as Ni,²⁷ Cu²⁸ and Fe²⁷ or a ceramic such as TiN²⁹ and TiC³⁰. The materials were usually ball milled with Si powder to finely disperse Si into the matrix. Besides, some Si containing compounds/alloys such as FeSi_2 , NiSi_2 ³¹ and SiO ³² have also been investigated as LIB anodes. Upon the first lithiation/de-lithiation cycle, the inactive element (Fe, Ni, O) was displaced by Li^+ , giving rise to elemental metal (Ni, Fe) or inactive compound (Li_2O) that formed buffering matrix. However, such Si-inactive composites usually showed quite low reversible capacities, which was attributed to poor Li^+ diffusivity in the inactive matrix that limits reaction of Li with Si.⁴

(b) Active matrix

In this type of composites, both active and matrix materials are active against Li^+ . So far, several Si-metal composites such as Si-Mg,³³ Si-Ag³⁴ and Si-Sn³⁵ have been investigated. It was found that these Si-metal alloys exhibited very poor cycling performance. However, when a third inactive

element was introduced to form complex active-inactive matrix, very good cycling performance could be achieved.⁴

One Si composite that attracts intensive research attention is Si-C. There are several benefits associated with carbon matrix. First, carbon is highly conductive, which can be used to effectively improve the low conductivity of Si. Second, carbon is lightweight and soft. Therefore, carbon matrix is able to accommodate the big volume change of Si without compromising the energy density of Si anodes much. Third, carbon chemistry including its preparation methods and electrochemical properties is well-known. Fourth, a carbon coating on Si surface was found to promote the formation of a stable SEI. Up to now, various preparation methods for Si-C composites have been reported, e.g. pyrolysis from polymers,³⁶ thermal decomposition of carbon containing gases,³⁷ ball milling,³⁸ etc, each of them having both advantages and drawbacks. Pyrolysis and thermal deposition methods are very flexible in the choice of precursors, but they require very high processing temperatures and result in non-uniform composition in the Si-C composites. On the other hand, the ball milling method is capable of controlling particle sizes and produces composites with good homogeneity. But the produced composites had a large initial irreversible capacity.⁴ Therefore, to achieve improved electrode structure, the two methods were combined.³⁹ In addition to the above methods, Si-C composites prepared from chemical reaction of gels have also been demonstrated.⁴⁰ Generally, Si-C composite anodes usually showed apparent

improvement in capacity retention over pristine Si anodes. Si-C is, up to now, the most successful and attractive Si composite anode.

(c) New binders

The conventional binder used in LIBs is PVDF, a thermoplastic material with poor elastomeric properties. A more elastomer binder was expected to be more capable of accommodating the huge volume change of embedded Si particles. Employing an elastomeric binder of styrene butadiene rubber (SBR), Liu *et al.* demonstrated Si powder based anodes with significantly improved cycling performance, compared to that with PVDF binder.⁴¹ Dahn's group showed that cross-linking the agent and adhesion promoter could enhance mechanical properties of PVDF binders, leading to improved performance.⁴² Unexpectedly, it was also found that stiff and brittle binders such as sodium carboxymethylcellulose (CMC)⁴³ and lithium polyacrylate (Li-PAA)⁴⁴ gave rise to even better performance than the elastomer binders. Several mechanisms have been proposed to explain these findings, e.g. CMC was believed to produce a more homogeneous dispersion and networking;⁴⁵ the formation of a strong chemical bond between the binder and Si could be another reason.⁴⁶

2.6.3.2 Si thin film

Amorphous Si thin film anodes are usually prepared by direct deposition of a Si thin film on current collectors by physical vapor deposition (PVD) or chemical vapor deposition (CVD). The advantages of Si thin film anodes are mainly attributed to two factors. First, the small film thickness results in a short Li^+ diffusion length, a high electrical conductance and a small internal stress during lithiation/de-lithiation. Second, the strong adhesion between the deposited film and its current collector maintains good contact during volume changes induced by lithiation/de-lithiation of Si.^{4 10 47} Therefore, Si thin films usually exhibit excellent electrochemical performance. For example, a 50 nm thick Si thin film deposited on nickel substrates showed an initial capacity of 3750 mA h g⁻¹ and a reversible capacity of near 3800 mA h g⁻¹ after 200 cycles at 1 C. Even at a very high discharge rate of 12 C, the 50 nm Si thin film still maintained a reversible capacity of as high as 3100 mA h g⁻¹ after 100 cycles.⁴⁸

However, active material loading of such Si thin film anodes is too low for practical applications. When the thickness of Si film was further increased to improve materials loading, the electrochemical performance drastically degraded. Li and his co-workers studied morphology changes of Si thin films of various thicknesses.⁴⁹ They found that when Si film thickness was small enough (e.g. ~100 nm), no cracks were observed after electrochemical cycling, the stress induced by volume change only caused surface roughness of the Si thin film. However, when its thickness exceeded a critical value (100-200 nm

according to their calculation), the Si film fractured into islands separated by cracks after cycling. Moreover, dimension of the Si pieces decreased with film thickness. To study the cracks formation mechanism in Si thin films, Sethuraman *et al.* measured stresses in a Si thin film by monitoring the substrate curvature changes during lithiation and de-lithiation with a multi-beam optical sensor wafer curvature system.⁵⁰ It was found that upon lithiation, a compressive stress was generated in the film due to the constraint of the substrate. The compressive stress increased fast during initial lithiation process and reached an elastic limit, after which further lithiation did not lead to further increase of the compressive stress, indicating the initialization of plastic deformation of the Si film. Upon de-lithiation, the compressive stress first decreased fast by undergoing elastic contraction, after which plastic deformation initiated to accommodate volume contraction of the Si film, as depicted in Fig. 2.11 below. The de-lithiation induced tensile stress in Si film eventually caused it to fracture into pieces.

Fig. 2.11 Stress evolution in the Si thin film during lithiation/de-lithiation (negative values represent compressive stress and positive represents tensile stress).⁵⁰

To improve electrochemical performance of thick Si films, porous Si with one-dimensional channels perpendicular to the Si film surface and Si pillar arrays comprised of standing alone Si islands were fabricated by electrochemical etching of a Si wafer⁵¹ and “island lithography” followed by dry etching of a Si film.⁵² The channels in the porous Si and the spacing between the Si pillars provided additional space to accommodate volume changes of the thick Si films. As a result, the porous Si and Si pillar arrays could tolerate the big volume changes and successfully retained their parent structures after cycling. Another interesting and effective approach to improve electrochemical performance of Si film anodes is to roughen the surface of current collectors to enhance the adhesion with Si film. So far, several methods including sanding,^{53, 54} etching⁵⁴ and electrolytic deposition⁵⁴ have been

demonstrated. After surface roughening, the improved adhesion between Si film and substrate current collector led to evident cycle life improvement. For example, a 3.6 μm thick Si film deposited on an electrolytically modified Cu substrate showed a reversible capacity of 2000 mA h g^{-1} for 50 cycles at 0.5 C.⁵⁴ In addition to the above methods, Si alloy films have also been widely investigated. The Si alloy films could be prepared by either using an alloy target or co-sputtering two or more material targets. A good sample is a multi-layered Fe-Si thin film anode prepared by sequential deposition of Si and Fe on a Cu or Ni substrate, as shown in Fig. 2.12a.⁵⁵ The annealed multi-layered Si thin film showed very stable cycling performance (Fig. 2.12b). After 300 cycles, no cracks were observed on the annealed Fe-Si film. The mechanism of stress migration in such Si alloy films is very similar to previous multi-phase Si components.

Fig. 2.12 (a) TEM image of the annealed Fe-Si multi-layer film and, (b) cycling performance of the Fe-Si film.⁵⁵

2.6.3.3 Si nanostructures

To deal with pulverization caused by the volume change in alloy electrodes, various models have been developed to study evolution of strain induced fracture during lithiation/de-lithiation processes. For example, Huggins and Nix presented a simple one-dimensional model and applied Griffith-Irwin relation to predict a material-specific critical size below which fracture does not occur.⁵⁶ Aifantis *et al.* treated active sites as nanospheres embedded in an inert matrix and employed linear elastic fracture mechanisms to predict the critical size to prevent fracture.⁵⁷ Christensen and Newman developed a mathematical model to describe volume expansion and contraction of a spherical insertion material as well as stress distribution due to Li^+ intercalation.⁵⁸ Deshpande and his co-workers developed a mathematical model relating surface energy with diffusion-induced stresses in nanowire electrodes and pointed out that surface energy and surface stress play important roles in diffusion induced stresses.⁵⁹ All the models predict that nanostructures are more resistant to volume change induced fracture than their bulk or micron sized counterparts and that for various Si structures such as particles and nanowires, there exists a critical size below which fracture does not occur. The predictions have been successfully verified by recent *in situ* and *ex situ* electrochemical investigations. Liu *et al.* performed *in situ* TEM investigation on lithiation of individual crystalline Si nanoparticles and found that those with diameters less than 150 nm showed no cracking or pulverization.⁶⁰ Ghassemi *et al.* conducted *in situ* lithiation/de-lithiation observation of individual amorphous Si nanorods and observed no

cracking in nanorods with a diameter of 26 nm.¹³ Ryu *et al.* performed *ex situ* TEM observation of crystalline SiNWs and found the critical diameter for pulverization is in the regime of 220-260 nm.⁶¹ Although the critical sizes observed in these experiments are not consistent with theoretically predicted values, the advantages of nanostructures in strain relaxation are quite consistent.

In addition to the improved strain accommodation capability, nanostructures also exhibit superior rate performance because 1) the high electrode/electrolyte contact area leads to a high Li^+ flux across the interface and, 2) the nanoscale dimension greatly reduces transport lengths for both Li^+ and electrons. In recent years, a number of Si nanostructures have been successfully synthesized and demonstrated as LIB anodes. In the following part, some representative nanostructures including homogeneous SiNWs, Si nanotubes, and porous Si will be briefly introduced to illustrate the benefits of employing nanostructures as LIB anodes.

(a) Homogeneous SiNWs

In 2008, Chan *et al.* directly synthesized crystalline Si nanowires (SiNWs) on a stainless steel (SS) current collector and used the SiNWs on the SS current collector as a LIB anode.⁶² The SiNW anode showed greatly improved performance over previous bulk or micron Si based anodes. In the first cycle, the anode achieved a lithiation capacity of over 4000 mA h g^{-1} . From the second cycle, both charge and discharge capacities remained nearly constant

for around 10 cycles. At a higher rate of C/5, the capacity was stable at $\sim 3500 \text{ mA h g}^{-1}$ for 20 cycles. The good performance could be attributed to several factors, as schematically illustrated in Fig. 2.13. First, thin SiNWs could easily release the stress induced by the change in volume through the surrounding space. Therefore, the SiNWs did not pulverize during lithiation/de-lithiation cycles. Second, the directly rooted SiNWs provide efficient charge transport pathways, promoting the capacity retention.

Fig. 2.13 Schematic of morphological changes of the SiNWs.⁶²

Later, Pribat's group found that owing to their volume change mismatch, the significant strain generated at SiNWs and current collector interface, could cause nanowire detachment during repetitive cycling and contributed to capacity fading. By controlling synthesis conditions, the group demonstrated

highly interconnected SiNWs (Fig. 2.14) that showed improved cycling performance.⁶³ The improvement was attributed to the connection between SiNWs so that even the detached SiNWs could retain their electrical connection with the current collector through the connected SiNWs.

Fig. 2.14 SEM image of the interconnected SiNWs.⁶³

The unique three-dimensional structure and stress-accommodating mechanism of SiNWs indicate possibly different lithiation/de-lithiation behaviors as compared to traditional Si particles or films. However, the results reported so far are quite contradictory. For instance, Liu *et al.* constructed an electrochemical device consisting of a single SiNW anode, an ionic liquid electrolyte, and a LiCoO_2 cathode inside a TEM to perform a real-time study of charging/discharging behavior of individual nanowire electrodes. They found that the final lithiation phase $\text{Li}_{15}\text{Si}_4$, as observed in Si particles and thick Si

films was not formed in un-doped SiNWs. In addition, lithiation in un-doped SiNWs was in-complete, leaving a residual crystalline Si core.²² However, when the SiNW was doped or surface-coated with a carbon layer, lithiation of the SiNW was complete with formation of the $\text{Li}_{15}\text{Si}_4$ phase.²² On the contrary, Matthew *et al.* performed the same experiment and found that the $\text{Li}_{15}\text{Si}_4$ phase indeed exists in un-doped SiNWs.⁶⁴ In another report, Ghassemi *et al.* observed the formation of crystalline $\text{Li}_{22}\text{Si}_5$ phase in an individual amorphous Si nanorods at the end of lithiation.¹³

(b) Si nanotubes

The SiNW anode demonstrated by Chan could maintain stable performance for initial cycles but after 50 cycles, only ~60% of the initial capacity was retained.⁶² So the SiNWs still suffered from strain induced capacity loss during long term cycling. To further enhance strain relaxation, Song *et al.* fabricated arrays of sealed Si nanotubes through several steps: 1) growth of ZnO nanorod arrays on current collectors, 2) CVD growth of Si shell on the ZnO arrays and, 3) removal of the sacrificial ZnO templates.⁶⁵ Compared with SiNWs, the Si nanotubes could more effectively accommodate the volume change through the interior space and showed superior capacity retention and rate performance. At 0.05 and 0.2 C, over 80% capacity retention was achieved after 50 cycles. At 0.05, 0.1, 0.2, 0.5, 1 and 2 C, the Si nanotube anode showed a charge capacity of 3360, 3160, 2650, 2260, 1900 and 1490 mA h g⁻¹,

respectively. They also found that the synthesized Si nanotubes underwent highly anisotropic expansion, with small axial expansion and very large radial expansion. With the help of a theoretical modeling of such structures, they suggested that the anisotropy was caused by the unique tubular structure in which the large free inner and outer surfaces could more easily accommodate radial expansion than axial expansion.

Fig. 2.15 (a) Top view SEM images, (b) TEM images and, (c) cross-sectional SEM images of the Si nanotubes before lithiation (left), after lithiation (middle) and after de-lithiation (right).⁶⁵

In another report, Park *et al.* synthesized unsealed Si nanotubes by repetitive impregnation of an anodized alumina membrane (AAM) with butyl-capped Si solutions and drying (Fig. 2.16).⁶⁶ One inherent benefit of this technique was that the organic precursor in the Si solution would form a conformal carbon coating on both interior and exterior surfaces of the Si

nanotubes during high temperature drying process (Fig. 2.16e). The carbon coating led to a stable SEI on Si surface and therefore a very high first cycle Coulombic efficiency of 89% was observed. The Si nanotubes showed excellent cycling performance with capacity retention of 89% after 200 cycles at 1 C. At a very high rate of 5 C, a high charge capacity of 2878 mA h g⁻¹ was achieved. The excellent performance could be attributed to the very thin wall thickness (~40 nm) and the interior channel of the Si nanotubes that ensured highly effective strain relaxation. In addition, the large surface area of the Si nanotubes was another reason to the high rate performance.

Fig. 2.16 (a-c) SEM images, (d-f) TEM images of the Si nanotubes, edge of the outer wall and inner surface of the tube.⁶⁶

(c) Porous Si

In addition to the dimension reduction, sufficient free space is also desired in Si anode materials to accommodate the volume change. Kim *et al.* first examined this idea by synthesizing 3-D porous Si particles as anodes.⁶⁷ The porous Si was synthesized by mixing silica nanospheres with butyl-capped Si gel, calcinations and HF etching to remove the silica templates. The obtained porous Si particles were comprised of interconnected pores with a size of 200 nm and the wall thickness was around 40 nm (Fig. 2.17). The porous Si particles showed very good cycling performance. Capacity retention of as high as 99% and 90% over 100 cycles was achieved at 0.2 C and 1 C, respectively. The excellent capacity retention could be attributed to the very thin Si thickness and the abundant pores in the particles that effectively accommodated strain generated during lithiation/de-lithiation. In addition, the very thin and conformal carbon coating formed during calcinations also played a role by stabilizing the SEI and improving overall electrical conductivity of the thin Si particles.

Fig. 2.17 (a-d) SEM images of the 3-D porous Si particles, e) TEM image of the Si particle showing the thin C coating, f) Raman spectrum of the Si particles.⁶⁷

In a later report, Ozin's group demonstrated a Si inverse-opal macroporous film directly synthesized on current collectors with closely packed multi-layer silica spheres as the template (Fig. 2.18).²¹ They found electrochemical performance of the porous structure was severely restricted by the electrical conductivity of Si. Amorphous Si only showed decent capacity retention at low rates. Conversion of amorphous Si to crystalline Si enhanced the conductivity and led to much better high rate performance, but the crystalline Si showed inferior capacity retention due to inhomogeneous volume changes. Finally, a Si-C composite material prepared by CVD coating of Si onto carbon inverse opals was found to show very good capacity retention and rate performance.

Fig. 2.18 SEM images of the fabricated Si inverse opal porous film.²¹

Major challenge of Si nanostructures

Although Si nanostructures are highly resistant to stress induced by the change in volume, their high surface areas also give rise to some negative effects. A prominent one is the exaggerated SEI. As introduced in Section 2.3, each electrolyte system has an electrochemical window that defines thermodynamic stable operating potential range of the electrolyte. Because the operating potential of Si falls outside the electrochemical window of common electrolyte systems, a SEI layer also forms on its surface during the first lithiation process. However, electrochemical behavior of the SEI on pristine Si anodes is vastly different from that on graphite anodes. The SEI on graphite anodes was found to be compact, smooth and stable during long term cycling, which largely contributes to the success of graphite anodes. On the other hand, the SEI on Si anodes is porous, rough and unstable.¹⁰ Moreover, the repetitive expansion-contraction of Si causes fracture of the SEI and exposes new Si

surface for SEI formation, as a result, the SEI would continuously grow as the battery cycles. The unstable SEI results in degraded performance of Si anodes through 1) continuous consumption of electrolyte and Li salts during SEI growth and, 2) increasing internal resistance of the battery because the SEI is electronically insulating. Therefore, the unstable SEI is identified as another important factor to cause poor cycling performance of Si anodes. Although the mechanical pulverization of Si anodes is greatly alleviated by employing Si nanostructures that are highly resistant to volume change induced stress, the unstable SEI problem remains unsolved and becomes more critical because of the large surface area of nanostructures.

Compositional analysis found that the SEI formed on graphite anodes is composed of Li_2CO_3 , alkyl Li carbonates (ROCO_2Li), LiF , ROLi , and polyethylene oxides, while the SEI on pristine Si anodes also contains significant amounts of fluorinated carbon and Si species, which could account for the different morphology of the SEIs on the two electrodes.⁶⁸ To solve this problem, current undergoing research mainly focuses on two directions, one is to passivate Si surface with a more stable material and the other is to modify composition of the electrolyte to promote the formation of a more stable SEI.

So far, the most successful and intensively investigated surface passivating material is carbon, due to its stable electrochemical property and some other advantages such as good electronic conductivity and versatile preparation techniques.^{69 70} Yen *et al.* investigated the compositional difference of SEI formed on pristine and carbon-coated Si powders in the electrolyte

containing LiPF_6 dissolved in the mixture of EC and ethylmethyl carbonate (EMC).⁶⁸ They found that the SEI on carbon coated Si was compact, smooth and contained siloxane species instead of fluorinated carbon or Si that were present in SEI on pristine Si. As a result, the carbon coated Si could maintain stable performance for 50 cycles while the pristine Si anode showed increasing irreversibility. Recently, atomic layer deposited alumina has been demonstrated as an effective surface passivating layer.^{71 72} On the contrary to carbon which is a very good electronic conductor, alumina is a good insulator. However, the transport of Li^+ across alumina layer seemed to be unimpeded. Liu *et al.* carried out an *in situ* transmission-electron-microscopy (TEM) observation of an Al nanowire with a native alumina surface layer and found that lithiation transformed the alumina into a stable Li-Al-O glass tube that could survive the volume expansion of ~100% of the Al core by undergoing elastic and plastic deformation.⁷³ Detailed working mechanism of the alumina coating on Si surface has not been investigated yet, but a similar mechanism could be expected.

As introduced in Section 2.3, the composition of SEI depends strongly on both electrode materials and electrolyte compositions. Therefore, the composition of electrolytes could also be modified to achieve a stable SEI. For instance, early attempts to employ graphite anodes were frustrated by the reduction reaction at graphite/electrolyte interface. Later, it was found that incorporation of EC into the electrolyte promoted the formation of a compact

and stable SEI layer that could help to achieve kinetic stability of graphite anodes. So far, several electrolytes including fluoroethylene carbonate (FEC), vinylene carbonate (VC) and several silane-based additives have been reported. Choi's group found that by adding 3% of FEC to the common electrolyte system (LiPF_6 dissolved in EC/DEC), a less porous SEI containing stable compounds was achieved. The more stable SEI led to obviously improved electrochemical performance of the Si anode with 88.5% capacity retention after 80 cycles and over 99% Coulombic efficiency up to 80 cycles. In contrast, the retention rate was only 67.9% for electrodes without FEC.⁷⁴ Xie's group found that in VC containing electrolyte, a smooth and uniform SEI was formed on Si surface. The uniform SEI layer was impermeable to electrolyte and its impedance was quite stable. In such VC containing electrolyte, the Si electrode showed significantly improved cyclability with 50% capacity retention after 500 cycles. In contrast, charge/discharge capacities of Si electrodes in VC free electrolyte dropped fast after only 100 cycles.⁷⁵

2.6.3.4 Voltage control

In addition to the above methods, another very effective approach to improve cycling performance of Si anodes is to limit charge/discharge cutoff voltages. By increasing the lower (or reducing the upper) cutoff voltage to restrict the amount of Li^+ inserted (or extracted), volume change of Si can be suppressed to achieve significantly improved cycling performance. Another

benefit of voltage control is elimination of the two phase change during charge/discharge. As mentioned in Section 2.6.1, a sudden phase change from amorphous Si into crystalline $\text{Li}_{15}\text{Si}_4$ occurs when lithiation proceeds to ~ 50 mV or below, and the subsequent de-lithiation process causes the crystalline $\text{Li}_{15}\text{Si}_4$ phase to amorphize. The inhomogeneous volume change associated with this phase change results in a very high internal stress and accelerates structural damage of Si anode.^{14 25} Therefore, by limiting the lower cutoff voltage to above 50 mV to avoid this phase change, structural stability of Si anodes could be much improved. However, the shortcoming of this voltage control approach is the significant reduction of electrode capacity. A representative example is shown in Fig. 2.19, where a narrower operating voltage window definitely results in a smaller capacity. Moreover, voltage control is difficult to implement in real applications.

Fig. 2.19 Cycling performance of a Si anode with different charge/discharge voltage ranges as indicated.

Chapter 3

Si-Ni cone arrays anode

3.1 Introduction

Our investigation of Si anodes began with Si thin films directly deposited onto metallic current collectors, which could be regarded as the simplest form of Si electrodes. The mechanics and electrochemical behavior of Si thin film anodes have been well addressed in Chapter 2. A common behavior of all Si thin films is that their capacities and rate performance degenerate fast beyond a critical thickness of ~200-300 nm as thicker films could build up the stress much easier. It is well known that the fracture of Si films is mainly caused by the volume change of Si in plane with the substrate due to the mechanical constraint of the substrate. In comparison, the volume change of Si perpendicular to the plane is less detrimental. This scenario is supported by the fact that even thick Si films would fracture into islands adhered to the substrate instead of pulverizing into powders.⁴⁹ Therefore, the key to achieve a high performance Si film anode is to properly handle the in-plane stress. A

straightforward and effective strategy is to pattern the Si film into separated pillars so that the in-plane stress does not accumulate over a long distance, as demonstrated by Green *et al.*⁵² Another strategy that we would expect to be effective is to manipulate the geometry of Si film to promote its volume change perpendicular to plane and therefore, suppress the detrimental in-plane stress. In this chapter, we demonstrate a novel Si-Ni cone array and investigate its electrochemical performance as LIB anodes. The structure is realized through self-assembly of vapor-deposited Si with a monolayer of Ni particles adhered to the Cu foil current collector as the heterogeneous nucleation centers. The spherical interface with the supporting Ni particle forces the Si coating to expand/contract in radial directions of the Ni particle and, therefore, suppresses the volume change in the plane of the current collector.

3.2 Experimental processes

Fig. 3.1 presents a schematic of the fabrication processes and structure of the Si cone array. Firstly, a monolayer of well-spaced Ni particles was synthesized on the Cu foil current collector. Si deposition was then carried out in a sputtering system. During deposition, the vapor phased Si nucleated on Ni particles and developed unique cone shaped morphology.

Fig. 3.1 Schematic of fabrication processes and structure of the Si cone array anode.⁷⁶

3.2.1 Dewetting

A piece of thin Cu foil, which is the conventional current collector for LIB anodes, was used as the substrate. In a typical process, the Cu foil substrate was sequentially cleaned in acetone, isopropyl alcohol (IPA) by ultra-sonic to remove the surface contaminations and then dipped in a diluted HCl solution to remove the surface oxide layer. After washed with deionized water and dried using N₂, the Cu foil was loaded into an electron beam evaporator (Auto 306, HHV) to deposit a thin film of Ni at a vacuum level of 10⁻⁶ torr. The dewetting process was carried out in an oven (blue M, Lindberg) at 600-800°C for ~5 mins in a mixture of Ar/H₂ environment.

Unfortunately, early attempts failed to produce Ni particles because the high processing temperature caused alloying of Ni thin film with Cu substrate. Indeed, in previous reports on dewetting of metal thin films,^{77 78} the substrate

was usually a flat silica that did not suffer from the alloying problem. To solve this problem, a barrier layer between Cu and Ni is needed. It has been suggested that several materials including TiN, Ta and TaN could probably work as the barrier layer. After several testings, we decided to employ TiN, an extremely hard ceramic material that is highly electrical conductive but electrochemically inert against Li^+ .⁷⁹ The TiN barrier layer was prepared in a magnetron sputtering system (ELITE RF/DC magnetron sputtering) in which a Ti target was DC sputtered in a mixture of Ar/N₂ (30/40 sccm) for ~5 mins at the power of 400 W. After introducing the thin TiN barrier layer, the issue of alloying of Ni with Cu was found to be successfully solved.

3.2.2 Si coating

In the next step, Si was deposited onto the Cu foil current collector decorated with Ni particles in the ELITE sputtering system operating in RF mode. The Cu foil was placed onto the sample holder which rotated at a constant speed of 25 r/min to promote uniform deposition. After the chamber was evacuated to the pressure range of 10^{-7} torr, pure Ar gas was introduced into the chamber at a flow rate of 200 sccm, a pure Si target (99.999%, Super Conductor Materials, Inc.) was sputtered at the power of 200 W for 100 mins. As a control sample, bare Cu foil was placed on the sample holder together with the Cu foil decorated with Ni particles during Si evaporation to realize a conventional Si thin film anode. The thickness of Si film, measured using a

surface profiler on a Si wafer placed beside the Cu foil, was confirmed to be ~500 nm. The mass loading of Si was determined by weighing the Cu foil substrate just before and immediately after Si deposition.

3.2.3 Compositional and morphological characterization

Raman spectroscopy (WITec Raman system) was used to access structure of the Si coating. A laser operating at $\lambda = 633$ nm was used as the excitation source. Energy-dispersive X-ray spectroscopy (EDX) was performed using an Oxford EDX equipped in conjunction with a field-emission scanning electron microscope (SEM) (LEO 1550 Gemini). To investigate electrode morphology after cycling, the half cells were disassembled in a fully delithiated state in a glove box filled with pure Ar (Innovative Technology, Inc. $\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm). The working electrode was immersed in propylene carbonate (PC) solvent overnight to completely remove the residual Li salts. The electrode was then transferred to a vacuum oven and heated at 80-120°C for several hours to remove the PC solvent.

3.2.4 Half-cells assembly

For electrochemical characterizations, the Si-Ni anode was assembled into CR2032 half-cells in the glove box. Customized rounded pure Li foil and a Celgard 2300 membrane were used as the counter electrode and separator,

respectively. The electrolyte was conventional LiPF_6 (1.0 M) dissolved in ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume). The half-cell was assembled by sequentially placing the working electrode, separator, lithium foil, SS spacer and spring spacer into the cathode shell (Fig. 3.2). After introducing several droplets of electrolyte, the battery was closed by the anode shell and crimped in a compact hydraulic crimping machine (MSK-110, MTI Corporation) (Fig. 3.3). The assembled half-cell (Fig. 3.4) was then unloaded from the glove box and aged for a whole night before subjected to electrochemical tests. The above assembly process was also used for the following experiments and will not be redundantly described in the following chapters.

Fig. 3.2 Components of a CR 2032 half-cell.

Fig. 3.3 MSK-110 hydraulic crimping machine.

Fig. 3.4 As assembled CR 2032 half-cell.

3.2.5 Electrochemical characterization

Galvanostatic charge/discharge cycles were performed to determine charge/discharge capacities, cycling performance and rate performance of the Si anodes using a battery tester (NEWARE BTS-5 V, Neware Technology Co., Ltd., China). As Si is an anode material, the test started from discharge (lithiation) followed by charge (de-lithiation). During discharge, a load connected to the two ends of the cell was continuously tuned by the tester to cause a constant current flow from the working electrode (Si) to the counter electrode (Li foil), causing the cell voltage of the half-cell to gradually decrease to the lower cutoff (0.01 V for our case). During the following charge process, the same current was forced to flow from the counter electrode to the working electrode by the tester, causing the cell voltage to increase gradually until the upper cutoff voltage was reached to finish the first galvanostatic cycle. Such discharge/charge processes were then repeated for desired times to obtain cycling performance of the anode.

Cyclic voltammetry was carried out using a multi-channel electrochemical workstation (AUTOLAB, M 101) at a scan rate of 0.1 mV s^{-1} . When the test started, the voltage of the half-cell was slowly ramped down to the lower cutoff of 0 V at a rate of 0.1 mV s^{-1} . The process caused Li^+ in the electrolyte to alloy with the Si and therefore corresponded to a lithiation process. After that, the voltage was slowly ramped up to the upper cutoff of 1.2 V at 0.1 mV s^{-1} , this process corresponded to a de-lithiation process. The steps were then

repeated to obtain cyclic voltammogram (CV) curves of the Si anode for several cycles.

3.3 Results and discussion

3.3.1 Electrode structure

Fig. 3.5 presents an SEM image of the Cu foil substrate after the dewetting process, showing a monolayer of well-spaced Ni particles with typical diameters of ~150 nm. In our experiment, we chose Ni as the dewetting material because it is electrochemically inert against Li^+ and therefore could maintain structural stability during electrode lithiation/de-lithiation processes. Dewetting method is employed here because it is scalable, cost-effective and relatively simple, compared to other methods, say lithography, etc. Another advantage associated with the dewetting method is that the synthesized metal particles usually exhibit very good adherence with the underlying substrate such that they are robust enough to endure the significant strain in Si anodes. We found that even after strong ultra-sonic treatment, the Ni particles could still remain bonded to the current collector.

Fig. 3.5 SEM image of the obtained well-spaced Ni particles on TiN coated Cu foil.⁷⁶

Fig. 3.6 (a and b) show top- and cross-section view SEM images of the obtained Si cone arrays. During Si deposition, the Ni particles functioned as nucleation sites for heterogeneous nucleation and therefore, the vapor phase Si elements preferentially nucleated at the Ni particles to minimize effective surface energy. As deposition proceeded, the deposited Si gradually developed into cone shaped shells supported by the Ni particles, instead of forming a continuous thin film as occurred on a flat substrate. In Fig. 3.6a, the boundaries between the intimately contacted Si cones are well distinguishable, some voids between the cones could also be observed. Fig. 3.6b shows that the Si cones are strongly rooted on the TiN coated substrate through the intermediate Ni particles. In addition, some Si flakes are observed between the Si cones. Such flakes are inevitable because small amounts of Si elements would also fall onto the interstitials between the Ni particles during deposition.

Fig. 3.6 (a) top-view, and (b) cross-section SEM images of the fabricated Si cone arrays.⁷⁶

Fig. 3.7 (a and b) present energy-dispersive X-ray (EDX) and Raman spectra of the Si-Ni anode, respectively. In the EDX spectrum, a very strong Si peak is observed, as expected. In addition, Cu, Ni and Ti peaks originating from the Cu foil, Ni particles and TiN barrier layer are also present. The absence of N peak is probably caused by the small mass of N atoms that is difficult for the

EDX system to detect. In the Raman spectrum, three broad spectra centered at ~ 155 , 330 , and 480 cm^{-1} and a weak shoulder at $\sim 400\text{ cm}^{-1}$ are the typical features of amorphous Si, attributed to TA (transverse acoustic), LA (longitudinal acoustic), TO (transverse optic) and LO (longitudinal optic) phonons, respectively.⁸⁰ The absence of the characteristic crystalline Si peak at $\sim 520\text{ cm}^{-1}$ confirms the amorphous structure of the deposited Si. Actually, amorphous Si is preferred over crystalline Si as LIB anodes because an amorphous structure would expand/contract homogeneously during lithiation/de-lithiation processes, leading to a small stress gradient and therefore better cycling performance.³⁵ On the other hand, the lithiation in crystalline Si was found to be crystallographic orientation dependent, leading to anisotropic volume changes in the first cycle and therefore accelerated capacity fade.⁸¹ In the Raman spectrum, a very weak peak at $\sim 900\text{ cm}^{-1}$ indicates the presence of trace amount of SiO_2 , which is probably developed during sample transfer. Surface oxidation is inevitable because amorphous Si could be oxidized within minutes upon exposure to air. In our experiments, the samples are always stored in the glove box immediately after Si coating and weighing to keep samples consistent.

Fig. 3.7 (a) EDX and, (b) Raman spectra of the Si anode.⁷⁶

3.3.2 Electrochemical performance

Electrochemical behavior of the Si-Ni cone array anode was first examined by cyclic voltammetry. Fig. 3.8 shows CV curves of the anode in the voltage range of 0-1.2 V vs. Li/Li^+ for the first 4 cycles. The first cycle CV curve indicates that the alloying of Li^+ with Si anode starts at ~ 0.5 V, below which the cathodic current gradually increases until the 0 V cut-off potential is reached. The process corresponds to the lithiation of amorphous Si to form amorphous Li_χSi ($\text{Si} + \chi\text{Li} \rightarrow \text{Li}_\chi\text{Si}$). In the first de-lithiation process, a broad peak centered at ~ 0.5 V is observed, which could be attributed to the de-lithiation of Li_χSi to form amorphous Si ($\text{Li}_\chi\text{Si} \rightarrow \text{Si} + \chi\text{Li}$). From the second cycle onward, the CV curve shape changes significantly, which is a common behavior for all Si anodes. During lithiation, two new relatively sharp peaks at ~ 0.2 and 0 V replace the single broad peak in the first cycle. The two peaks are caused by the sequential lithiation of amorphous Si to form two amorphous lithiated Si with different Li^+ concentrations ($\text{Si} + \chi'\text{Li} \rightarrow \text{Li}_{\chi'}\text{Si}$, $\text{Li}_{\chi'}\text{Si} + \chi''\text{Li} \rightarrow \text{Li}_{(\chi'+\chi'')}\text{Si}$). During de-lithiation, a new peak at ~ 0.4 V appears and the peak at ~ 0.5 V becomes less pronounced. The two peaks correspond to the sequential removal of Li^+ from two amorphous lithiated Si to form amorphous elemental Si ($\text{Li}_{(\chi'+\chi'')}\text{Si} \rightarrow \text{Li}_{\chi'}\text{Si} + \chi''\text{Li}$, $\text{Li}_{\chi'}\text{Si} \rightarrow \text{Si} + \chi'\text{Li}$).²⁵ It is also noted that as battery cycles, the cathodic peak at ~ 0.2 V slightly shifts to higher potential and the anodic peak at ~ 0.4 V slightly shifts to lower potential. This phenomenon indicates a reduced polarization effect, which could be attributed to the activation and reconstruction processes occurring in Si anode and at

electrode/electrolyte interface.²¹ The CV curve shapes obtained are consistent with previous reports on amorphous Si anodes.^{52 21}

Fig. 3.8 CV curves of the Si anode for the first 4 cycles.⁷⁶

Charge/discharge capacities and cycling performance of the Si-Ni anode were determined by galvanostatic cycling over the potential range of 0.01-1.5 V vs. Li/Li^+ . In the first cycle, a relatively low current density of 0.05 C (1 C corresponds a current density that fully charges or discharges theoretical capacity of all active materials in the electrode within 1 hour. For Si, 1 C=4200 mA g^{-1}) was applied to activate the electrode. For the following cycles, the current was maintained at 0.1 C. In this experiment, all capacities obtained are

calculated based on the mass of Si only. Fig. 3.9 presents voltage profiles of the Si anode for the 1st, 2nd and 40th cycle. During the first battery discharge (lithiation) process, the voltage quickly drops to ~0.5 V, after which a short plateau is observed. The plateau arises due to the formation of SEI during the first lithiation process. After that, the profiles show typical sloping charge/discharge behavior of Si. In the first cycle, the Si-Ni anode achieves a lithiation and de-lithiation capacity of ~3500 and 3070 mA h g⁻¹, respectively, corresponding to a Coulombic efficiency of 87.5%. The irreversibility of 12.5% is mostly caused by the formation of SEI that consumes Li⁺ in the electrolyte and generates very stable Li⁺-containing compounds such as Li₂CO₃. In such compounds, the Li⁺ cannot be extracted during the following de-lithiation process, resulting in less Li⁺ extractable from the anode than the amount previously intercalated. Therefore, quite large first cycle irreversibility is usually observed on all Si anodes.

Fig. 3.9 Voltage profiles of the Si anode for the 1st, 2nd and 40th cycle.

In the second cycle, the Si-Ni anode achieves a lithiation and de-lithiation capacity of ~ 2810 and 2750 mA h g^{-1} , respectively, giving rise to an efficiency of $\sim 98\%$. After that, the capacities remain quite stable, as shown in Fig. 3.10. At the end of the 40th cycle, a reversible de-lithiation capacity of 2635 mA h g^{-1} is still retained, corresponding to capacity retention of 95.7% , compared to the initial value at 0.1 C . The average fading rate is only 0.11% per cycle. In addition, a very high efficiency of over 99% is maintained from the 3rd cycle onwards.

Fig. 3.10 Charge/discharge capacities and efficiency versus cycle number of the Si anode.⁷⁶

For comparison, we also examined electrochemical performance of a Si thin film on a conventional flat Cu foil current collector with no Ni particles. The two electrodes have identical Si loadings because they were placed together onto the sample holder during Si coating. Both types of electrodes are tested at the same rate of 0.1 C over the same potential range. In a sharp contrast to the Si-Ni cones anode that shows stable performance over cycles, a fast capacity fading is observed for the Si thin film anode, as shown in Fig. 3.11.

Fig. 3.11 Cycling performance of the Si thin film anode.⁷⁶

The excellent cycling performance of the Si-Ni anode indicates a very stable structure of the Si cone arrays. To confirm this point, the half cells were disassembled in de-lithiated state after 20 cycles and examined using scanning-electron-microscopy (SEM). Fig. 3.12(a) presents a SEM image of the Si-Ni anode after cycling. It clearly shows that the Si cone arrays still remain bonded to the substrate without being detached. In addition, some cracked have developed to help release the stress in the electrode. In contrast, the Si thin film has broken into many small pieces and most have detached from the substrate, as shown in Fig. 3.12(b).

Fig. 3.12 SEM images of (a) Si-Ni anode and, (b) Si thin film anode after cycling.⁷⁶

The markedly different electrode morphologies after cycling clearly verify the superiority of the Si-Ni cone array structure in strain relaxation, compared to the Si thin film. We speculate that the good structural stability of the Si-Ni anode could result from following several factors. First, the Ni particles synthesized through high temperature dewetting process possess very good contact with the underlying TiN coated Cu foil and work as a concrete

mechanical support and efficient electron conductive pathways to the top Si cones. Second, the unique core-shell structure of the Si-Ni composite with a decreasing Si coating thickness from top to bottom favors expansion/contraction of the Si shell along radial direction of the Ni core, as schematically illustrated in Fig. 3.13. Therefore, the in-plane stress that is mainly responsible for pulverization of Si thin films is partially transferred to out-of-plane directions where there is more space to accommodate the volume changes. Third, compared to a continuous Si thin film, the Si in the Si-Ni anode is segmented into many cones whose boundaries could be used to release internal stress accumulated in the whole structure without necessarily damaging the Si cones. This point can be verified by performing a close inspection of the electrode after cycling (Fig. 3.12a), revealing that the cracks actually initiated and progressed along such boundaries, while the Si cone morphology remains unchanged.

Fig. 3.13 Schematic of working mechanism of the Si-Ni cone.⁷⁶

For future LIB electrodes, high rate performance is highly desired so that more powerful electronics could be powered. This is especially important for HEV applications that require high output currents and fast battery charge. Therefore, rate performance of the Si-Ni anode was also evaluated. To do this, the charge/discharge current was sequentially increased from 0.2 C and the battery was galvanostatic cycled at each rate for 10 cycles. Fig. 3.14 depicts variation of charge/discharge capacities and efficiencies versus cycle number of the Si-Ni anode up to 5 C. Remarkably, the Si-Ni anode exhibits quite good rate performance. At 0.2, 0.5, 1, 2, 3, 4 and 5 C, the anode achieves a charge (de-lithiation) capacity of ~2640, 2340, 2040, 1800, 1690, 1520 and 1300 mA h g⁻¹, respectively. The capacities at each rate are also quite stable with little fluctuation within the 10 cycles tested. Fig. 3.15 shows voltage profiles of the anode for the last cycle at each rate, showing typical sloping behaviors of Si anodes. Beyond 5 C, the capacities faded quite fast, indicating operating limit of the electrode. It should be noted that 5 C (21 A g⁻¹) means fully charging or discharging theoretical capacity of the battery within only 12 minutes. In the test, it took only 4 minutes to fully charge or discharge the battery because the de-lithiation capacity the Si-Ni anode achieves at 5 C is ~1300 mA h g⁻¹, which is ~1/3 of the theoretical value. For comparison, theoretical capacity of graphite, which is the anode material for commercial LIBs, is 372 mA h g⁻¹.

Fig. 3.14 Rate performance of the Si-Ni anode.⁷⁶

Fig. 3.15 Voltage profiles of the anode for the last cycle at the corresponding rates.⁷⁶

To our knowledge, very few Si nanostructures have been evaluated at such high rates before our report. For example, pristine Si nanotubes showed a capacity of 1490 mA h g^{-1} at 2 C ,⁶⁵ inter-connected crystalline SiNWs achieved 700 mA h g^{-1} at 5 C ,⁶³ alumina coated Si-Cu nanocables reached 790 mA h g^{-1} at 14 A g^{-1} .⁷¹ It is well known that high rate performance requires both a good

electronic conductivity to facilitate fast electrons transport and a good ionic conductivity to enable fast Li^+ transport across the electrode/electrolyte interface and in the electrode material. Therefore, we suggest that the inferior rate performance of previously reported Si anodes could probably be constrained by slow transport of electrons. This is because Si remains amorphous after first lithiation and, therefore, exhibits poor electronic conductivities. The Si nanotubes and inter-connected SiNWs are only connected to the current collectors at one end so that the transport of electrons from the tip to the current collectors is rather slow. Indeed, employing a metallic coating on Si to enhance its overall electronic conductivity has been shown to be very effective in improving rate performance of the Si anode.²³ Although the rate performance demonstrated by the Si-Ni cone array structure is not the best,⁶⁶ it is still better than most Si nanostructures previously reported.

3.4 Summary

LIB anodes based on Si cone arrays have been demonstrated and evaluated. The Si cone structure is realized through heterogeneous nucleation of Si on well-spaced dewetted Ni particles adhered to TiN coated Cu foil substrate. In this Si-Ni composite, the robust Ni particles function as concrete mechanical support and efficient electron transport pathways to the Si coating. The spherical contact with the Ni particle allows the Si cone to expand/contract radially to favor volume change in out-of-plane directions and suppress the detrimental in-plane expansion/contraction. As a result, the novel Si cone array anode could more effectively accommodate stress generated during lithiation/de-lithiation cycles and achieves much improved capacity retention and rate performance, compared to Si thin film anodes.

Chapter 4

CNT-Si core-shell nanowires anode

4.1 Introduction

New LIB electrode materials with high theoretical capacities (e.g. conversion and alloy materials) usually suffer from poor electrical and ionic conductivities because of the significant structural changes during cycling. This drawback limits energy efficiency and especially power capabilities of the materials. Nanostructuring has been identified as an effective approach to deal with this problem owing to the short diffusion length in nanomaterials. However, conventional slurry coating technique to prepare electrodes largely compromises advantages of nanomaterials because of the introduction of supplementary interfaces between active materials.⁸² To preserve the benefits of nanostructuring, new electrode configurations were introduced by Martin *et al.*⁸³ Instead of following the traditional materials mixing and slurry coating processes, they directly grew nanostructured active materials onto plane current collectors using a membrane template. Later, Simon's group demonstrated a novel Cu nano-architected electrode in which Cu nanorods were electro-

plated onto a plane Cu current collector and Fe_3O_4 was then electro-deposited on to the Cu nanorods to form a Fe_3O_4 shell-Cu core electrode (Fig. 4.1).⁸² This novel electrode configuration resulted in a 6-fold improvement in power density over planar electrodes.

Fig. 4.1 Cross-sectional view of Cu nanostructured current collector before and after Fe_3O_4 deposits.⁸²

Following Simon's concept, Cui's group demonstrated the first core-shell SiNW anode. They developed a one-step chemical-vapor-deposition (CVD) process to synthesize crystalline-amorphous core-shell SiNWs standing on a SS current collector.⁸⁴ As the lithiation of crystalline and amorphous Si occurs at different potentials, the amorphous Si shell could be selectively used to reversibly react with Li^+ while preserving the crystalline Si core by limiting the charging potential above the amorphization potential of crystalline Si (~ 120 mV) (Fig. 4.2). The intact crystalline Si core functioned as a stable mechanical support and an efficient 1-D electrical conductive pathway for the amorphous Si shell. The core-shell SiNWs demonstrated high charge capacity

($\sim 1000 \text{ mA h g}^{-1}$) and excellent capacity retention of 85% over 100 cycles at 0.2 C with a cut-off potential of 150 mV.

Fig. 4.2 (a) SEM and (b) TEM images of the core-shell SiNWs after cycling with cutoff of 150 mV, the crystalline Si core is successfully preserved. (c) SEM and (d) TEM images of the core-shell SiNWs after cycling with cutoff of 10 mV, the crystalline Si core has been amorphized.⁸⁴

Later, the same group demonstrated a core-shell SiNW with carbon nanofibers (CNFs) drop-casted or slurry-coated on a SS current collector as the core nanowires.⁸⁵ The CNF cores exhibit better structural stability and electrical conductivity than the crystalline Si cores and, no potential cut-off is required. Therefore, the core-shell nanowires show much higher charge capacities of $\sim 2000 \text{ mA h g}^{-1}$.

Fig. 4.3 (a) SEM and (c) TEM images of the CNFs before Si coating. (b) SEM and (d) TEM images of the CNF-Si core-shell nanowires.⁸⁵

After that, a few core-shell SiNWs employing different core materials have been demonstrated. Guan and his co-workers fabricated vertically aligned Cu-Si core-shell nanowires with electro-deposited Cu nanowires as the core.⁸⁶ Cao *et al.* synthesized randomly aligned Cu nanowires through thermal oxidation of Cu foil followed by reduction of CuO nanowires into Cu nanowires.⁷¹ Wang's group demonstrated assembled virus templates coated with Ni as the core nanowires.⁸⁷ In addition, NiSi, TiC and CNT sponge *etc.* have also been investigated as core nanowires.^{88 89 90} However, the results of these reports are quite scattered and the core-shell nanowire structure is still less exploited and much efforts are needed to be dedicated to this field. For instance, it is not hard to tell that the essence of such core-shell nanowires is a Si thin film coated on a three-dimensional current collector decorated with nanowires.

Advantages of core-shell SiNWs stem from the greatly enhanced effective surface area of the current collector so that a very thick Si film on a conventional plane current collector could be accommodated by such a nanowires-decorated current collector with a very thin Si coating, which definitely shows better electrochemical performance than a thick Si film.

However, it should also be noted that all core-shell SiNWs demonstrated so far showed much inferior electrochemical performance compared to Si thin film of comparable or even thicker thickness supported by a plane current collector. For example, Takamura *et al.* showed that a 50 nm thick Si thin film on a flat nickel foil current collector could achieve a high capacity exceeding 2000 mA h g⁻¹ and superior cyclability of over 1000 cycles at a rate of 12 C.⁹¹ On the other hand, most pristine core-shell SiNWs could hardly maintain stable performance up to 100 cycles. As the difference between Si thin films and core-shell SiNWs lies in their different current collector structures, it is therefore reasonable to deduce that structures of the core nanowires (alignment, spacing, wire diameters, etc) play critical roles in such core-shell nanowires.

Unfortunately, although many works on core-shell nanowires have been demonstrated, most are dedicated to synthesis of new core nanowire materials and very few tried to investigate the effects of core nanowire structures. A major obstacle to this research is lack of a synthesis technique that is capable of producing core nanowires with controllable morphology. Most of the reported

core nanowires were synthesized employing thermal CVD processes that usually produce randomly aligned thin nanowires. We believe that electrochemical performance of core-shell nanowires could be substantially improved by refining core nanowire morphology to more effectively relax strain generated. For example, it is accepted that a Si thin film on a flat current collector is subjected to stresses in both in-plane and perpendicular-to-plane directions, owing to the expansion/contraction of the Si film in the corresponding two directions. In a core-shell SiNW, the two stresses correspond to the axial and radial stresses, respectively. Meanwhile, curvature of the core nanowire introduces another stress---hoop stress, which does not exist in Si thin films. Therefore, core nanowire diameter could be an important factor that determines electrochemical performance of core-shell SiNWs. Actually, it has been suggested that the formation and growth of nanopores in the Si shell, which is responsible for capacity fading in the structure, are driven by the axial and hoop stress in the nanowire.⁹² Recently, Wang *et al.* performed *in situ* TEM investigation of lithiation/de-lithiation of single core-shell SiNWs and observed crack propagation in the Si shell driven by the hoop stress.⁹³ To alleviate the hoop stress, core nanowires with relatively large diameters are desirable due to the associated smaller curvature.

Another structural difference between Si thin films and core-shell SiNWs is free space distribution, which directly affects volume change accommodation in Si anodes. A Si thin film has sufficient space above the surface to accommodate volume change perpendicular to plane and to gain

sufficient access to electrolyte. On the other hand, free space distribution in core-shell SiNW anodes is dependent on nanowire alignment and spacing etc. Randomly aligned nanowires result in some locations with insufficient space to accommodate the big volume change of Si, e.g. crossovers and nanowire roots. Therefore, we expect that vertically grown nanowires would be more desirable owing to the associated relatively uniform free space distribution. In addition, sufficiently large inter-wire spacing is definitely necessary in volume change accommodation.

For our proof-of-concept study, we synthesized vertically aligned carbon nanotubes (CNTs) directly rooted on current collectors through a plasma enhanced CVD process (PECVD) and investigated electrochemical performance of CNT core-Si shell wire arrays.

4.2 Experimental processes

Fig. 4.4 Fabrication processes of the CNT-Si core-shell nanowires anode.

Fig. 4.4 shows a schematic of the fabrication processes of the CNT core-Si shell nanowires anode. Generally, two steps are involved to realize the structure. The first step is synthesis of vertically aligned CNT array on a stainless steel (SS) current collector and the second step is Si coating on the CNT backbone.

4.2.1 Vertically aligned CNT array

A stainless-steel (SS) substrate was sequentially cleaned in acetone, IPA and deionized water and then loaded into an electron beam evaporator to deposit a thin layer of Ni as the catalyst. The substrate was then transferred into a PECVD system (NANOINSTRUMENTS) to grow CNTs. In a typical growth process, the chamber was firstly evacuated to $\sim 2 \times 10^{-2}$ mbar by a mechanical pump. Ammonia (NH_3) was then introduced into the chamber at a flow rate of 240 sccm as the protecting gas. The chamber temperature was fast ramped up to 800°C at a rate of 200°C per minute. After stabilizing for 1-2 minute, plasma

was initiated, the power was gradually increased to 120 W and allowed to stabilize for another 2 minutes. Acetylene (C_2H_2) was then introduced into the chamber at a flow rate of 60 sccm to start the growth process which lasted for ~10 minutes. During growth, the chamber pressure was maintained at 8 mbar.

4.2.2 Si coating

After the growth of CNTs, a Si shell was coated onto the CNTs in another fully automated PECVD system (Cello AEGIS-20). Silane (SiH_4) balanced with nitrogen (N_2) was used as the precursor gas ($SiH_4:N_2=50:160$). The growth temperature was $200^{\circ}C$ and the chamber pressure was maintained at 400 mTorr. The deposition rate calculated on a Si wafer is 1 nm/sec. The Si mass was determined by weighing the substrate before and immediately after Si deposition using an analytical balance (Mettler Toledo XP 26, 0.002 mg).

4.2.3 Characterization

The half-cells assembly, electrochemical and Raman characterization steps are well described in Section 3.2. For TEM characterization, the CNT-Si array on SS substrate was removed from the substrate using a tweezer and dissolved in pure ethanol. The solution was ultra-sonicated for 5-10 minutes to separate the CNT-Si wire bundles and form a uniform dispersion. The solution was then stepwise dropped onto a carbon coated Cu grid and dried to finish the sample. TEM images were then obtained using JEOL 2010 at an accelerating voltage of 200 kV.

4.3 Results and discussion

4.3.1 Electrode structure

Owing to their high thermal stability, thermal conductivity and high current carrying capacity, vertically aligned, high density CNT arrays have triggered intensive research in interconnect applications in recent years.⁹⁴ PECVD is the most popular method to synthesize such vertically aligned CNTs because it can produce CNT arrays with an extremely high density and the location of CNTs can be precisely controlled by patterning catalyst metal with CMOS compatible lithography processes. During growth, the catalyst film is firstly dewetted into particles whose size determines diameter of the final CNTs. Therefore, the diameter and spacing of the synthesized CNTs can be controlled through several parameters such as catalyst film thickness, dewetting temperature and duration etc. In our experiment, a Ni film of ~20 nm thick was used to obtain CNTs with relatively large diameters and spacing. Fig. 4.5 below shows an SEM image of the fabricated CNT array. From the image, it can be seen that the CNTs are vertically aligned and exhibit quite large diameters. Although some quite thin CNTs could be observed, most CNTs exhibit diameters of ~150 nm. In addition, the inter-wire spacing is also quite large. The Morphology of the obtained CNT arrays here is distinctly different from the CVD-prepared nanowires in literature.

Fig. 4.5 Tilted angle SEM image of the CNT array fabricated.⁹⁵

Fig. 4.6 shows a TEM image of a typical CNT core-Si shell nanostructure. The CNT core exhibits a clear herringbone structure, consisting of stacked cone segment shaped graphite basal plane sheets with a non-zero orientation angle (θ) between the graphite basal planes and the tube axis.⁹⁶ The structure is suggested to be attributed to the high ratio of hydrogen atoms in the precursor gas.⁹⁷ In short, CNTs form by precipitation of graphene planes on catalyst particle surface. As dangling bonds are energetic and cannot exist at the edge of growing graphite planes, they must be capped during precipitation. Therefore, without hydrogen, the sp^2 -hybridized carbon orbitals (i.e. graphene basal planes) must point at the catalyst surface and form CNTs with concentric graphene planes ($\theta=0$). With hydrogen present in the growth gas, hydrogen can

cap dangling bonds at the edge of graphene planes to form sp^3 -hybridized carbons and allows free plane edges to be left behind. Plane formation then occurs by inter-conversion of the C-H moieties at the plane edge as carbon atoms are added to it. As a result, the CNT consists of stacked cones with $\theta > 0$.

Fig. 4.6 TEM image of a single CNT-Si core-shell SiNW.⁹⁵

In the TEM image, a rather smooth Si shell of ~60 nm thick on each side of the CNT, with a clear CNT/Si boundary can be observed. The diameter ratio of the Si-CNT to the CNT core is ~2:1. As the high CNT growth temperature (800°C) affects the weight of the SS current collector, the mass ratio of the CNT core to the Si shell is therefore calculated according to their

diameter ratio shown in the TEM image. From the image, the outer diameter of the CNT is ~150nm, diameter of the hollow inner is ~50nm (1/3 of the outer diameter) and diameter of the CNT-Si wire is ~270nm. The density of the solid graphitic wall is assumed to be the same as graphite (2.2 g cm⁻³) and the density of the amorphous Si prepared with our recipe is ~2 g cm⁻³, the mass ratio is calculated according to the formula

$$\text{Si:CNT} = \rho_{\text{si}}(\pi r_3^2 - \pi r_2^2) / \rho_c(\pi r_2^2 - \pi r_1^2) = 2.3:1,$$

where r_1 , r_2 and r_3 are the radius of the hollow inner, the CNT and the CNT-Si wire, respectively. ρ_{si} and ρ_c represent the densities of amorphous Si and graphite, respectively. Although this estimation is not very accurate, it does indicate that the content of CNTs to the overall CNT-Si composite is not dominant.

Fig. 4.7 below presents a top view SEM image of the CNT-Si core-shell wire array. After Si coating, distances between the wires are still quite large. This is quite important because lithiation induced volume expansion of the Si shell in such core-shell SiNWs is mainly along the radial direction as the axial volume change is constrained by the rigid core.⁹⁸ Therefore, a sufficiently large spacing is necessary to fully accommodate radial volume change of the Si shells.

Fig. 4.7 Top view SEM image of the CNT-Si core-shell array.⁹⁵

Fig. 4.8 shows the Raman spectrum of the CNT-Si composite. The spectrum is quite different from that prepared by sputtering, as discussed in Chapter 3 (refer to Fig. 3.7b). Here, a very sharp peak at $\sim 500\text{ cm}^{-1}$ is observed. It is well known that crystalline Si shows a very sharp peak at 520 cm^{-1} and amorphous Si shows a broad peak at $\sim 480\text{ cm}^{-1}$. Therefore, the peak at $\sim 500\text{ cm}^{-1}$ probably indicates a mixture of nano-crystalline Si embedded in amorphous Si, in consistent with previous reports on PECVD deposited Si.^{99 100} In addition, it is noted that a very weak peak at $\sim 900\text{ cm}^{-1}$ corresponding to SiO_2 is also present. We think the oxide is mostly developed during sample transfer and characterization process because such porous amorphous Si could be oxidized within several minutes in air. In our experiment, the samples are

usually transferred into the glove box immediately after fabrication to minimize oxidation.

Fig. 4.8 Raman spectrum of the CNT-Si composite.⁹⁵

4.3.2 Electrochemical performance

Electrochemical behavior of the CNT-Si anode was first characterized using cyclic voltammetry. Fig. 4.9a displays CV curves of the anode for the first 4 cycles, obtained at a scan rate of 0.1 mV s^{-1} . The curve shapes are quite different from that of the Si-Ni cone array (refer to Fig. 3.8), probably caused by the different electrode structures and Si preparation methods. For the CNT-Si core-shell anode, two peaks at ~ 0.2 and 0 V are observed during the first

lithiation process. Although most Si anodes only show a single peak at 0 V, the peak at 0.2 V has also been reported by several groups. Liu's group observed this peak in their Si-mesocarbon composite anode and attributed it to the lithiation of Si-C composite.³⁸ Chen's group also observed this peak in their Si nanospheres anode.¹⁰¹ Pollak *et al.* found this peak in their Si thin film electrodes and suggested two possible mechanisms, irreversible lithium trapping and reaction of Si dangling bonds.¹⁰² Kumta and Cui obtained a sharp peak at ~0.2 V in their differential capacity versus voltage curves and attributed it to the coexistence of two-phase structure of partially lithiated and un-lithiated amorphous Si.^{84 103} From the second cycle, another lithiation peak at ~0.4 V emerged, in addition to the two peaks at 0.2 V and 0 V. Although the peak at ~0.4 V has been observed in several reports, its mechanism is not clear.^{72 104 105} More investigation is needed to identify its phase and composition. In the anodic branch, the two peaks are related to the sequential de-lithiation of two amorphous Li_xSi ,²⁵ similar to the Si-Ni cone arrays anode in Chapter 3. As the battery cycled, the two peaks eventually merged into a single broad peak.

Fig. 4.9 CV curves of the CNT-Si core-shell wires for the first 4 cycles.⁹⁵

Charge/discharge capacities and cycling performance of the CNT-Si anode are determined by galvanostatic cycling over the potential range of 0.01-1.2 V at 0.2 C (1 C=4200 mA g⁻¹). In this experiment, all capacities are calculated based on the mass of Si only to reveal quality of the CNT core. The CNTs are treated as an inactive material because their contribution to capacities is very small, which will be demonstrated in later part. Fig. 4.10a shows charge/discharge capacities and Coulombic efficiencies of the CNT-Si anode. In the first several cycles, charge/discharge capacities and Coulombic efficiencies of the anode gradually increase. The phenomena can be attributed

to an activation process involving reconstruction and activation of Si and electrode/electrolyte interface, which is also reflected by the unstable CV curves with gradually increasing currents in Fig. 4.9. In the 7th cycle, the anode achieves the maximum de-lithiation capacity of 2755 mA h g⁻¹, after which the capacity remains quite stable. At the end of the 80th cycle, a de-lithiation capacity of 2510 mA h g⁻¹ is still retained, corresponding to a capacity retention of 91% in comparison with its maximum value. In addition, the anode maintains a very high Coulombic efficiency of over 99% after the first 3 activation cycles. Fig. 4.10b displays typical voltage profiles of the anode in a full charge/discharge cycle (after the 7th cycle), showing typical sloping behaviour of Si anodes.

Fig. 4.10 (a) Variation of charge/discharge capacities of the CNT-Si anode versus cycle number, (b) typical charge/discharge voltage profiles of the CNT-Si anode.⁹⁵

The highly stable cycling performance and high efficiency demonstrated indicate that the CNT-Si core-shell nanowires could effectively accommodate strain generated and maintain stable structures during battery cycling. To further confirm structural stability of the CNT-Si composite, a half cell was disassembled in fully de-lithiated state after 50 galvanostatic cycles for SEM and TEM inspections. As shown in Fig. 4.11, even after so many cycles, the electrode still maintains its original morphology. Tips of the CNT-Si wires stick together because of the surface tension force of the PC solvent during drying. In addition, a film, which is probably the SEI, has developed on the surface of the

structure. Fig. 4.12 shows a TEM image of a single CNT-Si core-shell wire after 50 cycles. Compared to the pristine wire before cycling (Fig. 4.6), the Si shell seems to be brighter so that the contrast between Si and CNT is not as clear as before. This is reasonable because the repetitive insertion and removal of Li^+ would inevitably causes Si to become more porous so that the initially dark Si shell appears brighter after cycling. Another apparent structural change is that the initially smooth Si surface becomes rougher after cycling with a thin layer of highly porous film developed on the surface. The porous surface film is believed to be the SEI. Due to the de-lithiation which caused a significant volume contraction, the SEI formed during previous lithiation process is usually broken and new surfaces are then exposed for SEI formation. Therefore, the SEI would continuously grow as the battery cycles and eventually glue the CNT-Si wires into bundles, as observed in Fig. 4.11. When the CNT-Si wires were removed from the substrate and dispersed in ethanol to prepare samples for TEM inspections, we found it was very hard to obtain a uniform dispersion by ultra-sonic treatment. The suspension was therefore treated with strong ultra-sonication for about 30 minutes before being dropped onto the copper mesh. Even though, we found most CNT-Si wires were still in bundles, very few separated wires could be observed. The strong ultra-sonic process could also have contributed to structural damage of the SEI. However, the most important result shown here is that the Si coating was not pulverized and still remained strongly bonded to the CNT core after 50 cycles.

Fig. 4.11 SEM image of the CNT-Si anode in de-lithiated state after 50 galvanostatic cycles at 0.2 C.

Fig. 4.12 TEM image of a CNT-Si core-shell wire after 50 cycles.⁹⁵

We believe that the good structural stability of the CNT-Si anode could be attributed to several factors. First, the large diameter CNTs are robust enough to be free of damage caused by the stress at CNT-Si interface. In contrast, very thin metallic backbone was found to get bent or distorted after cycling.^{62 64} Second, the large CNT diameter reduces hoop stress in the Si shell, leading to less stress accumulation than those thin core nanowires. Third, the relatively large inter-wire spacing in the vertically aligned CNT-Si array can efficiently accommodate the lithiation/de-lithiation induced volume change of the Si shells. To further confirm the advantages of employing CNT core nanowires with large diameters and large spacing, we also fabricated CNTs with much smaller diameters and inter-wire spacing as the core simply by using a thinner Ni catalyst film of ~10 nm. Fig. 4.13a shows a tilted angle SEM image of the fabricated CNT array. In this case, the diameter and inter-wire spacing of the CNTs are obviously smaller, most CNTs exhibit diameters of ~50 nm. Fig. 4.13b shows a TEM image of a typical thin CNT-Si nanowire. The diameter of the CNT presented here is ~60 nm, which is significantly smaller than the CNT shown in Fig. 4.6. The diameter of the CNT-Si core-shell nanowire is ~120 nm, so the diameter ratio of Si coated CNT to the CNT core is ~2, very similar to previous thick CNT-Si wires.

Fig. 4.13 (a) SEM image of the thin CNT array and, (b) TEM image of a thin CNT-Si core-shell nanowire.⁹⁵

Fig. 4.14 below compares cycling performance of the thin CNT-Si wire array for the first 50 cycles with that of the thick CNT-Si wires. Both samples are cycled at 0.2 C over the same potential range of 0.01-1.2 V. For the CNT-Si anode with the thin CNT core, the capacity retention after 50 cycles is 91% of the maximum value. On the other hand, the retention rate of the thick CNT-Si wires is 96.4% over the same number of cycles, obviously better than the thin CNT-Si wires. It is worth mentioning that the results are repeatable, other samples also show consistent results, that is, CNT-Si wires with larger core diameters and larger inter-wire spacing exhibit better capacity retention.

Fig. 4.14 De-lithiation capacities of the CNT-Si anode with the thin CNT core in comparison with the thick CNT-Si anode.⁹⁵

In addition, another factor that contributes to the good cycling performance of our CNT-Si wire array is the strong bonding between the CNT core and Si shell. Previous *in-situ* TEM investigation on lithiation/de-lithiation

of a single carbon fiber-Si core-shell wire found that the Si coating could strongly adhere to the CNT core even if cracks had developed in the Si, which is consistent with our *ex-situ* TEM result (Fig. 4.12).⁹⁸ Kumta's group also demonstrated that a Si thin film anode with a carbon substrate showed much better structural stability and capacity retention than those with a traditional Cu foil substrate. They attributed the improvement to the better adherence of Si to carbon and the buffering effect of carbon substrate.¹⁰⁶ We noted that, previously, vertically aligned Cu rods with a relatively large diameter were fabricated as the core, but capacity retention of the Cu-Si core-shell composite was not as good as our CNT-Si composite.⁸⁶ The inferior adhesion between Cu and Si, compared with that of carbon and Si, is probably an important reason.

Rate performance of the CNT-Si anode based on thick CNT cores was also evaluated by sequentially applying a series of charge/discharge currents of 0.2, 0.5, 1, 2, 4, 8 and 12 C to the half-cells. As shown in Fig. 4.15, the de-lithiation capacity of the CNT-Si anode in the 10th cycle at 0.2 C is ~2670 mA h g⁻¹, in consistent with previous sample in Fig. 4.10a. At higher rates of 0.5, 1, 2, 4, 8 and 12 C, the corresponding de-lithiation capacity is ~2280, 2010, 1730, 1480, 1170 and 985 mA h g⁻¹. The capacity at 12 C (50 A g⁻¹) is more than two times that of theoretical specific capacity of graphite. Finally, when the charge/discharge current is reverted to 0.2 C, the de-lithiation capacity recovers to more than 2500 mA h g⁻¹, suggesting that the electrode structure is still preserved after the high rate tests.

Fig. 4.15 Rate performance of the CNT-Si anode.⁹⁵

The rate performance demonstrated here is superior to almost all core-shell nanowires previously reported. It should be noted that apart from a good electrode structural stability, good high rate performance also requires fast and efficient charge transport. Therefore, the good rate performance of the CNT-Si anode can be interpreted as follows. First, the robust CNTs directly rooted on current collectors provide efficient 1-D electron transport pathways to the Si shell. In Chapter 3, we suggested that rate performance of those SiNWs and Si nanotubes was mainly constrained by slow transport of electrons from the tip to the bottom current collector. The problem is successfully solved in the core-shell structure owing to the presence of highly conductive core nanowires. Second, the relatively thin Si coating greatly reduces charge transport lengths for both electrons and Li^+ , they only have to diffuse through the thickness of the Si shell to complete a charge (or discharge) cycle. The above two attributes are well-known as the major benefits of such core-shell nanowires. In addition, a special benefit associated with the vertical alignment and large inter-wire

spacing of the CNTs in our electrode is efficient access of electrolyte to the whole structure so that the whole Si coating, including those at the bottom of the array, can gain sufficient access to electrolyte. This feature effectively alleviates concentration polarization problem at high charge/discharge rates. The polarization could be quite severe in previous randomly oriented and dense core-shell SiNWs that have insufficient space to facilitate fast Li^+ transport from/to electrode surface to/from bulk reservoir during de-lithiation/lithiation processes. This improvement could be an important reason that contributes to the superior rate performance of the CNT-Si anodes to other core-shell nanowires anodes. Lastly, previous *in-situ* TEM investigation showed that due to the fast diffusion of Li^+ in carbonaceous materials, lithiation in such carbon core-Si shell nanowires occurred from both Si shell surface and carbon-Si interface, which eventually depleted the Si in the middle of the shell.⁹³ In other words, the carbon-Si interface also serves as fast Li^+ transport channels. This feature also indicates that a carbonaceous core nanowire is perhaps more advantageous in fast charge transport than electrochemically inert core materials such as copper.

Finally, as the CNTs are also electrochemically active against Li^+ and contribute to the observed capacity, their contribution is quantified by charging/discharging a CNT electrode without Si coating at the same current (e.g. both at 0.2 mA) as the CNT-Si electrode. This is reasonable because the PECVD process to synthesize CNTs is highly repeatable, therefore, both electrodes have similar amount of CNTs. Fig. 4.16 displays overall

charge/discharge capacities of the CNTs electrode at various charge/discharge currents (C refers to C_{Si}). The values were normalized by the mass of Si in the CNT-Si electrode to quantify the contribution of CNTs. The results clearly verify that the contribution of CNTs is very small and therefore, the capacities of the CNT-Si anode are mostly contributed by the Si shell.

Fig. 4.16 Overall charge/discharge capacities of the CNT electrode and the CNT-Si electrode at the same test currents.⁹⁵

4.4 Summary

CNT arrays consisted of vertically aligned CNTs with large diameters and large inter-wire spacing are synthesized on stainless-steel (SS) current collectors and investigated as core nanowires of core-shell SiNW anodes. The CNT-Si core-shell nanowire anode exhibits a good structural stability during lithiation/de-lithiation cycles and demonstrates excellent capacity retention and rate performance. The good electrochemical performance could be mainly attributed to the large diameters and large inter-wire spacing of the CNT core that lead to more effective strain relaxation and electrolyte access during battery charge/discharge, compared to the core-shell SiNWs reported elsewhere.

Chapter 5

CNT-Si core-shell nanowires with gradient Si shell morphology

5.1 Introduction

Although the CNT-Si core-shell wires demonstrated in Chapter 4 showed much improved capacity retention and rate performance over previous core-shell SiNWs, the structure could be further improved. For example, although cycling performance of the CNT-Si anode was quite stable for the first 80 cycles, the fading rate was obviously accelerated after 80 cycles, as shown in Fig. 5.1. Such behavior is inevitable for Si anodes because the huge volume change caused structural damage would gradually accumulate as battery cycles and no Si nanostructures could completely avoid such structural degeneration. For our CNT core-Si shell wires, the increased porosity of the Si shell after cycling (refer to Fig. 4.12) is a clear evidence of such structural damage.

Fig 5.1 Charge/discharge capacities of the CNT core-Si shell anode beyond 80 cycles.

To explore other possible causes to the accelerated capacity fading phenomenon, a half cell subjected to 120 cycles at 0.2 C was disassembled and inspected using an SEM. It is found that the CNT-Si wire array is covered by a very thick SEI film (Fig. 5.2), which is consistent with previous reports on pristine Si anode.⁶⁵ Compared to the electrode morphology after 50 cycles (Fig. 4.11), the SEI becomes much thicker and eventually shields the CNT-Si array. This finding further verifies that the SEI formed on pristine Si surface is not stable and would continuously grow as battery cycles.^{68 107} As introduced in Chapter 2, the unstable SEI would consume Li salts and is another cause to capacity fading of the CNT-Si anodes. Unexpectedly, we also observed few ruptures of the CNT-Si array film, as shown in Fig. 5.2. The rupture is unlikely to occur during cycling process because in that case, wire detachment should occur randomly and individually, instead of in large areas. We believe that such rupture is most likely to be caused during sample drying process. It's worth

mentioning that such severe structure damage was not observed in the sample completed only 50 cycles. But in another sample subjected to prolonged cycling, more such ruptures were observed. This phenomenon indicates that as battery cycles, the structural damage at the wire roots is continuously accumulated and gradually weakens the adherence of the CNT-Si array to the underlying SS substrate, which should account much for the observed accelerated capacity fading after 80 cycles.

Fig. 5.2 SEM image of the CNT-Si anode after 120 cycles.

The structural damage at the wire roots should be caused by the repetitive volume expansion/contraction of the Si coating at the wire roots and on the SS substrate surface. To solve this problem, we suggest that the

morphology of the Si shell can be engineered to reduce or eliminate the Si coating at the array bottom. By carefully designing the fabrication process, we realized a gradient Si coating whose thickness gradually decreases along the CNT core, as schematically illustrated in Fig. 5.3. Another potential benefit of employing the gradient Si shell is that it makes better use of the space distribution in the CNT core array. This is because the synthesized CNTs are not uniform in length (refer to the CNT array image in Fig. 4.5), so the density of CNTs actually increases from the top to bottom of the CNT array, resulting in a gradually decreasing free space. The gradient Si shell therefore caters to the space distribution and makes better use of the space to accommodate volume change of the whole Si shell.

Fig. 5.3 Schematics of the cone shaped CNT-Si core-shell wire array rooted on the current collector.¹⁰⁸

5.2 Experimental processes

The CNT array on SS current collector was fabricated as described in Section 4.2. To realize the gradient Si shell, a directional physical vapor deposition process (sputtering) was employed. During Si evaporation, the CNT array shadowed the amount of Si atoms (clusters) penetrated into the array bottom, giving rise to a gradient Si shell.

5.3 Results and discussion

5.3.1 Electrode structure

Fig. 5.4 shows a TEM and a dark field image of a single CNT-Si core-shell wire. Gradient morphology of the Si coating is quite obvious. In Fig. 5.4a, the thickness of the Si coating on the sidewall of the CNT core gradually decreases from over 100 nm at the tip to an undetectable thickness at the bottom. Another striking feature of the Si coating is that it consists of aligned Si plane sheets rooted on the CNT core, in a sharp contrast to the smooth and homogeneous Si coating prepared using CVD method. The unique structure is probably caused by the herringbone structure of the CNT core that consists of graphene basal plane sheets (refer to Fig. 4.6). As discussed in section 4.3.1, the hydrogen in the growth gas allows for the presence of graphene plane edges, it is very likely that during Si sputtering deposition, the graphene plane edges function as nucleation sites to promote the formation of the Si plane sheets.

Fig. 5.4 (a) TEM image of a CNT-Si cone shaped wire, (b) Dark field image of a CNT-Si cone shaped wire.¹⁰⁸

5.3.2 Electrochemical performance

Fig. 5.5 shows the CV curves of the gradient CNT-Si wires for the first three cycles at a scan rate of 0.1 mV s^{-1} . The CV curve shapes are nearly identical to that of the Si-Ni cone array discussed in Chapter 3 (Fig. 3.8). In the

first cycle, a broad peak near 0 V corresponding to the alloying of Li^+ with amorphous Si is observed in the cathodic branch. In the anodic branch, the two peaks at 0.38 and 0.5 V correspond to sequential removal of Li^+ from amorphous SiLi_x . From the second cycle onwards, two lithiation peaks at 0.2 and 0 V and two de-lithiation peaks at 0.35 and 0.5 V are distinguishable. The slight potential shift of the two de-lithiation peaks is caused by continuous electrode activation. However, it is noticed that the lithiation peak at ~ 0.2 V (for the first cycle) and ~ 0.4 V (for subsequent cycles) in previous PECVD coated CNT core-Si shell anode are not observed here. The phenomena suggest that Si coatings prepared with different methods exhibit different electrochemical characteristics.

Fig. 5.5 The CV curves of the gradient CNT-Si anode for the first three cycles.¹⁰⁸

Cycling performance of the gradient CNT-Si anode was evaluated by galvanostatic cycling over the same potential range of 0.01-1.2 V and at the same current density of 0.2 C as previous uniform CNT core-Si shell nanowire anode. In this experiment, the contribution of CNTs is also neglected and all capacities are calculated based on m_{Si} . Fig. 5.6a depicts the capacity retention performance of the gradient CNT-Si anode. The electrode achieves an initial de-lithiation capacity of 2768 mA h g⁻¹ in the first cycle. After that, the capacity slowly increases as the battery cycles and reaches the maximum value of 2812 mA h g⁻¹ at the 17th cycle. Thereafter, the capacity fades very slowly. The de-lithiation capacity at the 80th cycle is 2588 mA h g⁻¹, corresponding to capacity retention of 92% of the maximum value. The capacity retention for the first 80 cycles is slightly higher than previous uniform CNT core-Si shell wires (91%). However, the gradient CNT-Si nanowires anode does not show such accelerated capacity fading phenomenon after prolonged cycling as previous uniform CNT-Si nanowires anode. Fig. 5.6b presents the voltage profiles of the gradient CNT-Si nanowires anode for the 100th cycle, still showing typical sloping shapes of Si anodes.

Fig. 5.6 (a) Cycling performance of the gradient CNT-Si anode at 0.2 C and, (b) voltage profile of the gradient CNT-Si anode for the 100th cycle.¹⁰⁸

The long-term stable cycling performance of the gradient CNT-Si anode in this experiment indicates that the gradient Si shell has alleviated or even eliminated the wire roots structural damage. To further confirm this, the half-cell was disassembled after 120 cycles to examine structural stability of the CNT-Si wires. As shown in Fig. 5.7, the CNT-Si after cycling is covered by a quite thick SEI that glues the CNT-Si array into a film, similar to previous uniform CNT-Si anode. However, all the CNT-Si wires are still firmly adhered to the substrate and no ruptures could be found. In addition to the gradient morphology, the unique structure of the Si shell consisting of aligned Si sheets

standing on the CNT core could also contribute to the stable performance by accommodating volume change of Si through the space between the Si plane sheets. Nevertheless, the superior structural stability of the gradient CNT-Si anode strongly evidences the importance of structural engineering in core-shell SiNW anodes.

Fig. 5.7 SEM image of the gradient CNT-Si anode after 120 cycles.

High rate performance of the gradient CNT-Si core-shell wire array was also examined to assess whether the gradient Si shell morphology is also beneficial for high rate charge transport. Fig. 5.8a shows charge/discharge capacities and efficiency versus cycle number of the gradient CNT-Si anode during the rate performance test. The de-lithiation capacity retained in the last

cycle at the corresponding rates are 2515 (at 0.5 C), 2175 (at 1 C), 1833 (at 2 C), 1514 (at 4 C), 1149 (at 8 C), 910 (at 12 C) and 718 mA h g⁻¹ (at 15 C). When the charge/discharge currents were further increased to 20 C and above, the charge/discharge capacities and efficiencies fluctuated a lot, indicating operating limit of the CNT-Si anode. Fig. 5.8b presents the last cycle charge/discharge voltage profiles of the anode at the corresponding rates.

Fig. 5.8 (a) Lithiation/de-lithiation capacities and Coulombic efficiencies versus cycle number of the gradient CNT-Si wires during rate performance test, (b) voltage profiles in the last cycle at the corresponding rates.¹⁰⁸

The rate performance of the gradient CNT-Si core-shell wire array is superior to most core-shell SiNWs previously reported. However, it is not as good as the uniform CNT-Si core-shell sample demonstrated in previous chapter. Fig. 5.9 compares capacity retention of the two types of CNT-Si anodes at higher rates. Their capacities at 0.2 C are taken as their respective bases. At the rate of 12 C, the gradient CNT-Si anode retains ~32% of the capacity at 0.2 C, while the more uniform CNT-Si anode retains ~37%. The result somewhat contradicts our expectation that the gradient Si shell would show better high rate performance due to the increased space at the array bottom. By comparing structures of the two types of CNT-Si core-shell wires, we think the result can be interpreted as follows. In the sputtering-prepared graded Si shell (Fig. 5.10a), a very thick Si cap is generated due to the directionality of the sputtering process. The Si cap takes up quite a high ratio of the overall Si coating weight and is about 50% thicker than the cap of the PECVD prepared Si shell (Fig. 5.10b). Such comparison is reasonable because the CNT cores in both samples are similar in diameter. As the charge/discharge rate increases, the limited electronic conductivity or solid state diffusion of Li^+ in Si results in more and more incomplete lithiation/de-lithiation of the thick Si cap. Consequently, the capacity retention rate of the gradient CNT-Si anode degenerates faster than the uniform CNT-Si anode.

Fig. 5.9 Capacity retention of the two types of CNT-Si anodes at higher rates.

Fig. 5.10 TEM image showing cap of a) the gradient CNT-Si wire and, b) the uniform CNT-Si wire.

5.4 Summary

Vertically aligned CNT core-Si shell wires with gradient Si coatings are fabricated by using a directional sputtering deposition process assisted by the shadowing effect of the vertically aligned CNT core. The gradient Si shell eliminates Si coating at the CNT roots and on the underlying stainless-steel current collector surface. Consequently, the CNT-Si anode shows improved structural stability and demonstrates better cyclability than the uniform CNT core-Si shell anode in Chapter 4. The experiment further verifies the importance of rational structure engineering in core-shell SiNWs anodes.

Chapter 6

Controllable fabrication of SiNW arrays

6.1 Introduction

SiNW arrays have attracted intensive research in recent years owing to their very promising applications especially in energy storage and energy conversion, say in SiNW LIBs, photovoltaic (PV) applications, etc. In energy storage applications such as LIBs, SiNW arrays fabricated directly on a SS current collector have been shown to be capable of more effectively accommodating significant volume changes of Si during lithiation/de-lithiation processes and greatly improved electrochemical performance of Si anodes, compared to bulk or micron sized Si.⁶² In PV applications, SiNW arrays have been shown to exhibit extremely strong optical absorption in the solar spectrum. It is estimated that less than 1% equivalent of Si materials in SiNW arrays can achieve the same amount of absorption as traditional planar wafer-based PV devices. Therefore, SiNW arrays could greatly reduce raw materials cost of PV devices.^{109 110}

Basically, there are two categories of methods to fabricate SiNW arrays: bottom up and top down. Vapor-liquid-solid (VLS) is the most popular bottom up method. In a typical process, the catalyst which is usually gold is heated to a temperature higher than the Au-Si eutectic point, Si precursor which is usually SiH_4 decomposes on the catalyst surface and form liquid alloys with the catalyst. Si starts to precipitate and form one dimensional SiNWs when supersaturation is reached. In this method, the diameters of the SiNWs can be controlled through the catalyst sizes. By using SiCl_4 as the precursor, vertically aligned SiNWs have also been demonstrated.¹¹¹ However, a big problem with the VLS method is the catalyst contamination: at high temperatures, gold could diffuse into SiNWs and induce deep recombination centers. The recombination centers greatly degrade minority carrier life-time and diffusion lengths in the SiNWs, which is highly undesirable in PV applications. Moreover, the VLS process is known to be rather costly and impractical for large scale applications.

Opposite to the bottom up methods that join Si atoms to form SiNWs, top down methods prepare SiNWs by etching bulk Si. Reactive ion etching (RIE) is a microfabrication process that is frequently utilized to dig trenches in bulk Si. When combined with a high resolution lithography process, RIE can produce SiNW arrays with precise control over their dimensions and locations. The drawback of RIE methods is the limited aspect ratio achievable, especially when the SiNW spacing is small. Moreover, the combined lithography and RIE processes are also rather expensive for most large area applications.

Another newly developed top down method is metal assisted chemical etching (MACE).¹¹² In a typical process, a thin film of catalyst (Ag, Au or Pt) is firstly deposited onto a wafer surface using either electroless deposition or physical vapor deposition (sputtering, electron beam evaporation, thermal evaporation). After that, the catalyst coated Si wafer is immersed in an etching solution containing HF and an oxidizing agent such as H_2O_2 to perform etching process. During etching, the wafer beneath the catalyst is dissolved while the part without catalyst remains almost intact so that SiNW arrays comprised of high density SiNWs are fabricated. Although detailed etching process and mechanism are controversial, a general picture describing the etching process is suggested: 1) when a Si wafer loaded with catalyst is immersed into the etching solution, the oxidant such as H_2O_2 is preferentially reduced at the surface of the noble catalyst metal due to the catalytic effect of the metal. 2) The holes generated by the reduction reaction inject into the Si that is in contact with the catalyst and cause oxidation of Si. 3) The oxidized Si is etched by the HF in the solution and exposes new Si for oxidation. As the concentration of holes is at maximum at the metal/Si interface, the etching rate of Si beneath the catalyst is much faster than the bare Si. Therefore, the Si beneath catalyst is dissolved and the bare Si remains almost intact and form SiNWs.¹¹³ A representative SEM image of the fabricated SiNW array is as shown in Fig. 6.1.

Fig. 6.1 SEM image of the fabricated SiNW array using MACE method by our group.

Compared with the VLS and RIE methods, the MACE method is more cost-effective for large area applications and exhibits several distinct advantages. First, the etching process is carried out at room temperature, eliminating the high temperature induced metal contamination problem. Second, the etching direction is found to be affected by Si wafer orientation, etching temperature and etchant concentrations. Therefore, by tuning one or more of the parameters, slantingly aligned or even zigzag SiNW arrays could be readily obtained.¹¹⁴ Third, the etching process is interplay of injection of holes and dissolution of oxidized Si, if the rate of holes injection is higher than the dissolution rate, the excess holes will diffuse to side walls of the SiNWs and lead to porous SiNWs. Therefore, the porosity of SiNWs could be controlled by the etchant concentration.¹¹³ Finally, as SiNWs are obtained by etching bulk Si, their doping profiles are identical to the parent Si wafers, no extra doping

process is needed. The SiNWs obtained using this method are usually of high electronic quality. It should also be noted that for electronic applications, a main drawback of this solution based top-down etching method compared to the bottom-up methods is the roughening of SiNW surface, which causes large density of defect states and degenerates carrier mobility.

Unfortunately, although convenient and productive, the MACE method lacks effective control over the SiNW diameters and spacing. The fabricated SiNWs are always intimately contacted and there are many incompletely etched SiNW bundles. In some applications, parameters such as nanowire diameter and spacing actually play critical roles. Peng *et al.* investigated electrochemical performance of such SiNW arrays as LIB anodes.¹¹⁵ Huang and his co-workers coated a carbon shell on such SiNW arrays and demonstrated cycling performance up to 40 cycles.¹¹⁶ However, the capacity retention was not as good as the SiNW arrays synthesized through VLS method. The inferior performance was most likely caused by the poor spacing in such SiNW arrays that was not large enough to effectively accommodate the big volume change of Si during lithiation/de-lithiation cycles.

In the MACE process, the Si covered by the catalyst will be etched away while the part uncovered remains intact and form SiNWs. Thus, a straightforward approach to control diameters and spacing of the SiNWs is to pattern the catalyst metal to create well controllable size and density of nano holes on the metal layer. So far, several approaches have been developed to pattern the catalyst, including electron beam lithography (EBL),¹¹⁷ interference

lithography (IL),¹¹⁸ nanospheres^{119 120} and Anodic Alumina Membrane (AAM) masks¹²¹. The expensive EBL and IL methods are impractical for large area applications and therefore will not be addressed here. The nanospheres and AAM masks are briefly described below.

Nanospheres

A typical SiNW fabrication process employing nanospheres patterning is schematically illustrated in Fig. 6.2. Firstly, a closely packed monolayer of nanospheres (Polystyrene (PS) sphere or silica) was assembled on a flat Si wafer. Secondly, the dimension of the nanospheres was reduced through either RIE (for PS spheres) or HF solution etching (for silica spheres) to isolate the nanospheres. Thirdly, a catalyst metal film was deposited by physical vapour deposition. The deposited catalyst film formed a continuous metal mesh covering the Si substrate. Fourthly, the Si substrate was immersed into the etching solution to perform etching. The Si in direct contact with the catalyst metal mesh was dissolved. In contrast, the Si beneath the nanospheres was un-etched and forms SiNW arrays. In this method, the diameters of the SiNWs could be easily tuned by controlling etching time of the nanospheres. However, the drawback of this method is that it is rather difficult to assemble a large area continuous nanosphere monolayer, especially when the diameter of the nanospheres is less than 200 nm. Although wafer scale assembly of silica spheres with Langmuir–Blodgett technique has been demonstrated,¹²² the

assembly and transfer processes were rather complex and not easy to control, preventing practical applications.

Fig. 6.2 Schematic illustration of fabrication process of the MACE method combined with PS nanosphere patterning. (1) A mono-layer of polystyrene (PS) nanosphere was assembled on Si surface. (2) Reactive-ion etching (RIE) was used to trim diameters of the spheres. (3) Silver catalyst film was deposited onto Si surface. (4) A typical metal-assisted chemical etching process was carried out to form SiNW arrays.¹¹⁹

Anodic Alumina Membrane (AAM)

AAM membranes have been widely used as templates to fabricate various nanowires. Huang *et al.* firstly reported a modified metal-assisted chemical etching (MACE) method that employed an ultra-thin AAM membrane to pattern catalyst metal and realized well defined SiNW arrays.¹²¹ In a typical process (see Fig. 6.3 for illustration), an ultra-thin AAM membrane was fabricated and transferred to a Si wafer surface. A RIE process was then carried

out to transfer the channel patterns in the AAM membrane to the underlying Si wafer. After removing the AAM mask, catalyst metal was deposited onto the Si surface and formed a continuous metal mesh with the same pattern as the AAM mask. After that, a MACE etching process was carried out to etch away the Si covered by the catalyst metal mesh and obtain SiNW arrays.

Fig. 6.3 Schematic of the MACE process with an AAO mask to fabricate SiNW arrays. (a) An ultra-thin AAO membrane was first fabricated and transferred to a Si substrate. (b) A RIE process was employed to transfer pattern of the AAM to the Si substrate followed by the removal of the AAM. (c) A thin catalyst metal film was deposited onto the Si surface. Some metal was also deposited onto the bottom of the holes. (d) A typical MACE process was carried out.¹²¹

Later, they reported a simplified process. As schematically illustrated in Fig. 6.4a, after transferring the ultra-thin AAM mask to Si with the assistance of a polystyrene (PS) layer, catalyst metal was directly deposited onto the AAM surface to form a catalyst metal mesh. The whole structure was then immersed into the etching solution. During etching process, the ultra-thin AAM mask was first etched by the etching solution and the etching process then proceeded with the metal mesh as the catalyst.¹²³

Fig. 6.4 Schematic of the fabrication process. (a) An ultra-thin AAO membrane was firstly fabricated and transferred to a Si substrate, with polystyrene (PS) as the transfer media. A very thin Ag catalyst was then deposited onto the AAO surface. The whole substrate was then immersed into an etching solution to form SiNWs. (b) bird's eye view and (c) diameter distribution of the obtained SiNWs.¹²³

More recently, Kim and his co-workers developed another variation of the AAM patterning method.¹²⁴ Instead of transferring an ultra-thin AAM mask to the Si wafer, they first fabricated an extremely thin catalyst metal mesh floating on solution surface by depositing the catalyst metal on the surface of a very thick AAM template and subsequent etching of the AAM to release the metal mesh. The metal mesh was then transferred to the Si wafer surface and immersed in the etching solution to perform MACE etching, as schematically illustrated in Fig. 6.5.

Fig. 6.5 Schematic of the fabrication process developed by Kim. (a) An Ag-Au bilayer was deposited onto an anodic aluminium oxide (AAO) membrane. Here, the Ag was used as a catalyst for MACE etching and the Au was used to enhance mechanical strength of the Ag film during transfer and etching. (b) The Ag-Au bilayer was released by etching away the AAO substrate and floated on the solution surface. (c) A Si substrate was immersed into the solution to transfer the Ag-Au film onto Si. MACE was subsequently carried out to generate SiNW arrays.¹²⁴

Compared to the nanospheres patterning method, the AAM method is advantageous in fabricating SiNWs with very small diameters of less than 10 nm. However, the AAM method is complicated as transferring of the ultra-thin AAM membrane or the catalyst metal mesh, which is easily broken during transfer, is required. The complicated transfer process is highly undesirable for large scale applications. Moreover, current fabrication technique usually produces AAM membranes in cm^2 range, thus scalability is another challenge.

We have developed a simple catalyst patterning method with which we are able to produce large area SiNW arrays with controllable nanowire diameters and spacing at low costs. In this method, a monolayer of well-spaced

metal particles is synthesized directly on wafer surface and employed as the sacrificial mask to pattern the catalyst metal film.

6.2 Experimental processes

Fig. 6.6 Schematic of the fabrication procedure developed by us.

Fig. 6.6 illustrates the fabrication procedure we developed to fabricate SiNW arrays. An n-type or p-type Si wafer with (1 0 0) surface orientation was used as the starting material. The wafer was firstly sequentially cleaned in acetone and IPA by ultra-sonication for 10 minutes, respectively, to remove surface contaminations. After flushed in deionized water for several minutes to remove the residual IPA, the Si wafer was immersed in a piranha solution

(H₂SO₄ (98%): H₂O₂ (30%) =3:1) for about 30 minutes to remove surface greases. The wafer was then soaked in a tank with running deionized water for several minutes and blew dry with a nitrogen gun. The ultra-clean Si wafer was then loaded into an electron beam evaporator for Ag thin film coating.

In the next step, the Si wafer with a thin Ag film was annealed at 600-800°C for several minutes to transform the Ag thin film into a monolayer of well-spaced Ag particles. The process was carried out under an ambient atmosphere of pure Ar. After that, a Ti/Au bilayer was sequentially deposited on the Si wafer by e-beam evaporation. To form a continuous catalyst metal mesh, the sacrificial Ag particles were removed by ultrasonic treatment. Finally, the Si wafer was immersed in an aqueous etching solution containing HF and H₂O₂ to produce vertically SiNW arrays.

6.3 Results and discussion

Fig. 6.7 below shows a SEM image of the obtained monolayer of well-spaced Ag particles on Si wafer surface after the dewetting process. Although the Ag particles are not highly uniform in sizes, they are naturally well spaced and form a monolayer, so no extra transfer or size reduction steps are needed. Besides, the average diameter and spacing of the obtained Ag particles could be tuned through the thickness of the dewetting Ag film.

Fig. 6.7 SEM image of the obtained monolayer of well-spaced Ag particles on Si surface.

The process to obtain a catalyst mesh with the dewetted metal particles as the template turned out to be quite challenging. In an early attempt, we tried to obtain the catalyst mesh simply by dissolving the Ag particles in nitric acid after deposition of the Au catalyst. The method did not succeed because the aspect ratio (height/diameter) of the Ag particles was not high enough so that the deposited Au clusters falling on Si and Ag particles were connected to each other. After Ag was dissolved in nitric acid, the Au clusters on Ag particles still remained and covered the underlying Si. To solve this problem, we tried to remove the Ag particles together with their Au coatings by ultrasonic treatment. Unfortunately, the Au film was easily damaged by ultrasonic treatment due to its poor adhesion to Si. Therefore, an ultrathin Ti layer was introduced under

Au to enhance adhesion of the top Au layer to the Si wafer so that the Au film could survive the strong ultra-sonication process. Fig. 6.8 shows an SEM image of the obtained Au catalyst mesh, which has an opposite pattern to the Ag particles monolayer.

Fig. 6.8 SEM image of Au catalyst mesh on Si surface after removing the sacrificial Ag particles.

Finally, the Si wafer with the Au catalyst mesh was immersed in the etching solution to obtain SiNW arrays. Upon immersion, the underlying Ti layer was firstly dissolved by HF in the solution, causing Au mesh to directly contact Si. The etching process proceeded by continuously dissolving the Si in direct contact with the Au mesh, while the bare Si remained, forming SiNW arrays.

Fig. 6.9a shows a top view SEM image of the obtained SiNW array. The pattern of the SiNWs is exactly defined by the Ag particles. Fig. 6.9b shows a tilted angle SEM image of a large area SiNW array. Fig. 6.9c depicts a zoom-in image of the array. It clearly shows the standing alone SiNWs with good inter-wire spacing. In Fig. 6.9(b and c), the very thin and uniform Au catalyst mesh is clearly observed at the SiNW array bottom.

Fig. 6.9 (a) Top view, (b) tilted angle and, (c) zoom-in SEM images of the obtained SiNW array.

Compared with previously reported methods of catalyst patterning such as lithography, nanospheres and AAM, the method demonstrated here is definitely more advantageous in process simplicity, cost, repeatability and scalability, etc. In our method, the large area sacrificial metal particles are synthesized through a more reliable, repeatable and scalable *in-situ* dewetting process, which is more suitable for large area fabrication. In addition, the obtained metal particles are naturally well-spaced and in a monolayer form, no sphere trimming (as in nanospheres method) or pore widening (as in AAM methods) processes are needed. As the diameter and spacing of the obtained metal particles are directly proportional to the thickness of the initial Ag film, the nanowire diameter and inter-wire spacing of the SiNW array therefore can be controlled by adjusting the dewetting metal film thickness. Although our method is not for fabricating highly periodic SiNW arrays, it is highly useful in those applications where periodicity is not compulsory, say LIB anode applications.

The method presented here is not limited to produce vertically aligned SiNWs. Previous study of the MACE process has established a clear relation between Si etching direction and other parameters, such as Si wafer surface orientation, concentration and temperature of etching solution. Thus, by adjusting these parameters, slantingly aligned and even zigzag shaped SiNW arrays can also be realized.

Electrochemical performance of the as-fabricated SiNWs was simply evaluated by cyclic voltammetry. For this purpose, a very thin Si wafer of 100 μm was used as the substrate and well-spaced SiNW arrays of $\sim 20\ \mu\text{m}$ were fabricated using our developed method. The Si wafer was then cut into small pieces ($1\times 1\text{cm}^2$) and assembled into half cells following the steps described in section 3.2.4. Fig. 6.10 shows CV curves of the SiNW array anode obtained at a scan rate of $0.1\ \text{mV s}^{-1}$. The curve shapes are very similar to that of the vapor-liquid-solid (VLS) prepared SiNW arrays on SS substrate.⁶² In the first cycle, a very narrow lithiation peak near 0 V is observed. In the following lithiation cycles, this peak gradually becomes wider. In addition, a very small peak at 120 mV-150 mV is also present. This peak was attributed to the lithiation of Au catalyst.⁶² In the anodic branch, two peaks at $\sim 0.35\ \text{V}$ and $\sim 0.5\ \text{V}$ corresponding to the extraction of Li^+ from SiLi_x are present. As battery cycles, the peak at 0.5 V slightly shifts to higher potentials. Another obvious phenomenon is that both lithiation and de-lithiation current gradually increase with cycling. The phenomenon is believed to be caused by the thick Si substrate that is gradually activated as battery cycles and participate in lithiation/de-lithiation. Unfortunately, it is impossible to test charge/discharge capacities and cycling performance of the SiNW array because they will be greatly affected by the underlying Si substrate. A more advanced electrode configuration, which will be recommended in the final chapter of the thesis is needed.

Fig. 6.10 CV curves of the SiNW arrays anode.

6.4 Summary

A simple, reliable and scalable method to produce large area SiNWs with controllable diameters and spacing has been demonstrated. The method employs a dewetting process to synthesize a monolayer of well-spaced metal particles as the sacrificial template to obtain a large area catalyst metal mesh *in situ* on Si surface. Electrochemical performance of the obtained SiNW array as a LIB anode is also evaluated using cyclic voltammetry. Compared to previously reported methods, this method is easier to control and more scalable, therefore it exhibits very promising applications in many areas such as solar cells and lithium ion batteries.

Chapter 7

Summary and Future Work

7.1 Summary

➤ In Chapter 4, LIB anodes based on Si-Ni cone arrays composed of supportive Ni particles and cone shaped Si coatings have been demonstrated. The Si anode shows significantly improved cyclability compared to a conventional flat Cu foil supported Si film with the same Si mass loading. When cycled over the potential range of 0.01-1.5 V, capacity retention of 95.7% is achieved over 40 galvanostatic cycles at 0.1 C with an average fading rate of 0.11% per cycle. In contrast, the Si film anode with a flat Cu foil current collector could only maintain stable cycling performance within 20 cycles. Post-cycling electrode morphology investigation showed the Si-Ni cone array still adhere to its substrate with good structural stability while the Si film had cracked into pieces and only a small portion still adhered to its substrate. The superior performance of the Si-Ni cone array anode to the Si thin film anode could mainly be attributed to two factors. First, the Si is segmented into small islands so that the internal strain is not accumulated

over a long distance as in the Si thin film. Second, the spherical Ni support forces radial expansion/contraction of the Si coating to promote its volume change in out-of-plane directions and therefore suppress the more detrimental in-plane stress that is mainly responsible for the failure of Si films. The results obtained further confirmed that in-plane stress is major cause to the fracture and pulverization of Si film anodes. The method demonstrated here could use as an effective tool to mitigate the destructive in-plane stress generated during lithiation/de-lithiation of Si and improve capacity retention performance of such film-like Si anodes.

- In Chapter 5, LIB anodes based on vertically aligned CNT-Si core-shell wire arrays have been developed. In this core-shell structure, the CNTs are vertically aligned, well-spaced and exhibit quite large diameters and large inter-wire spacing. After 80 galvanostatic cycling at 0.2 C, the CNT-Si core-shell anode showed a high de-lithiation capacity of 2510 mA h g^{-1} with 91% capacity retention over 80 cycles. In addition, excellent rate performance upto 12 C was demonstrated. The electrochemical performance exceeded most core-shell SiNWs reported which usually employed thermal chemical vapour deposition processes to synthesis core nanowire arrays that had no control over nanowire diameters, spacing and orientations. The results clearly demonstrate the importance of structural engineering in core-shell SiNWs, which had never been reported before. First, core nanowires with larger diameters are more effective in strain accommodation, probably due to reduced hoop stress and better mechanical strength. This is in consistence

with previous calculation showing that the hoop stress contributed a lot to crack formation in Si shells. Second, sufficient inter-wire spacing is required to effectively accommodate volume expansion of Si shells and ensure sufficient access of nanowire array to electrolyte. Li^+ diffusion in electrode and across electrolyte/electrode interface is another limiting factor to good rate performance, in addition to good electronic conductivity. The excellent rate performance of our CNT-Si core-shell nanowires is contributed by both good electronic conductivity of the CNT-Si composite and effective Li^+ transport in the structure.

- In Chapter 5, the morphology of the Si shell on CNT cores is further engineered to circumvent excessive stress induced structural damage at wire roots and pursue better anode performance. A gradient Si shell whose thickness gradually decreases along the CNT core from top to bottom of the array is realized through a directional physical vapor deposition process in combination with the shadowing effect of the CNT array. The unique morphology eliminates Si coating at the bottom of the CNT array and effectively protects the wire roots from structural damage. Owing to this improvement, cycling performance of the CNT-Si core-shell wires is further improved.
- In Chapter 6, a novel method to fabricate aperiodic SiNW arrays with controllable nanowire diameter and spacing has been invented. The method employs an *in situ* dewetting process to transform a metal thin film on Si substrate to a monolayer of well-spaced metal particles. The metal particles

monolayer is then used as a sacrificial template to pattern the catalyst film into a mesh. A Ti adhesive layer under the catalyst film is used to protect the catalyst film from structural damage during the removal of the sacrificial catalyst metal particles by ultrasonic. Finally, SiNW arrays are obtained by performing solution etching of the Si substrate with the obtained Au mesh as the catalyst. When evaluated as a LIB anode, the SiNW array shows very similar CV behaviors with previously reported VLS prepared SiNW array on SS substrate. Compared to previously reported methods to fabricate SiNW arrays with controllable diameters and spacing, our method is more repeatable, scalable, cost-effective and easier to control.

7.2 Recommendations for future work

- The Si-Ni cone arrays show significantly improved cyclability compared to Si thin films. However, the initialization and propagation of cracks along the Si cone boundaries indicate that the volume change of Si is still not fully accommodated, due to the deficient space between the intimately contacted Si-Ni cones. In a sample subjected to prolonged cycling, some Si coatings were found to have detached from the Ni particles. It is suggested that the structure could be further improved by two ways. The first way is to improve the adherence of the Si coating to the Ni particles by either performing high temperature annealing or introducing an adhesive layer between Si and Ni. The second way is to refine the ratio of the Si coating thickness to the Ni

particle diameter to further enhance mechanics of the structure during charge/discharge.

- The CNT-Si core-shell wires demonstrated in this thesis strongly verifies the importance of structural engineering for core-shell nanowire anodes. It is suggested that more detailed investigations could be carried out to characterize this structure. For example, the conclusions presented in this thesis are derived from *ex situ* data. An *in situ* study could gain deeper insights into stress evolution in the structure. Another issue is that for practical application of the core-shell structure, electrochemical performance is not the only criterion. A practical energy density must also be fulfilled. With the core diameter fixed, a thinner Si shell definitely leads to better electrochemical performance. However, a thinner Si shell also results in a lower electrode energy density because of the lower Si material loading. Therefore, a detailed investigation is needed to find out the optimal ratio of Si shell thickness to core nanowire diameter that could maximize the Si loading without compromising the electrochemical performance much.
- In Chapter 5, the thick cap of the gradient Si shell is suggested to be the origin of the inferior high rate performance of the gradient CNT-Si anode to the PECVD prepared CNT-Si anode. A more detailed study could be carried out to clarify this point. For example, an *in situ* TEM experiment, as well described in several reports ⁹³ could be performed to observe lithiation/delithiation behaviour of the two structures to gain more insights into the

effects of Si shell morphology. The morphology of the gradient Si shell could also be further refined by improving fabrication processes.

- In Chapter 6, we tried to use the SiNW array on Si substrate as a LIB anode. However, the attempt was frustrated by the presence of the Si substrate that could greatly affect cycling performance of the SiNW anode. It is recommended to use a more advanced electrode configurations to solve this problem. One possible process is to employ a thin Si wafer with a pre-coated metallic backing and etch through the Si wafer until the metallic backing is reached. The metallic backing could work as the current collector to the SiNW array and more importantly, prevent fall-off of the SiNWs during etching. Another possible process is that after obtained the SiNW array on Si substrate, a polymer could be filtrated into the SiNW array to help transfer the SiNW array onto a metallic current collector and use the structure as a LIB anode. Moreover, current research on LIB polymer electrolytes makes it possible to employ a polymer electrolyte as both the transfer media and the electrolyte.

Author's Publications

Y. Fan, K. Huang, Q. Zhang, Q. Xiao, X. Wang, and X. Chen, Novel silicon-nickel cone arrays for high performance LIB anodes. *Journal of Materials Chemistry* 2012, 22 (39), 20870-20873.

Y. Fan, Q. Zhang, C. Lu, Q. Xiao, X. Wang, and B. K. Tay, High performance carbon nanotube--Si core--shell wires with a rationally structured core for lithium ion battery anodes. *Nanoscale* 2013, 5, 1503-1506.

Y. Fan, Q. Zhang, Q. Xiao, X. Wang, K. Huang, High performance lithium ion battery anodes based on carbon nanotube-silicon core-shell nanowires with controlled morphology. *Carbon* 2013, 59, 264-269.

Q. Xiao, **Y. Fan**, X. Wang, R.A. Susantyoko, and Q. Zhang, A multilayer Si/CNT coaxial nanofiber LIB anode with a high areal capacity. *Energy & Environmental Science* 2014, 7, 655-661.

C. Lu, **Y. Fan**, H. Li, et al. Core-shell CNT-Ni-Si nanowires as a high performance anode material for lithium ion batteries. *Carbon* 2013, 63, 54-60.

Y. Liu, K. Huang, **Y. Fan**, et al. Binder-free Si nanoparticles@carbon nanofiber fabric as energy storage material. *Electrochimica Acta* 2013, 102, 246-251.

Y. Liu, K. Huang, **Y. Fan**, Q. Zhang et al. Three-dimensional network current collectors supported Si nanowires for lithium-ion battery applications. *Electrochimica Acta* **2013**, 88, 766-771.

X. Wang, **Y. Fan**, R.A. Susantyoko, Q. Xiao, L. Sun, D. He, and Q. Zhang, Mesoporous Co₃O₄ nanosheet networks for ultra large areal capacity Li ion battery anodes. *Nano Energy*, accepted.

Q. Xiao, Q. Zhang, **Y. Fan**, X. Wang, and R. A. Susantyoko, Soft silicon anode for lithium ion batteries. *Energy & Environmental Science*, under revision.

X. Wang, R. A. Susantyoko, **Y. Fan**, L. Sun, Q. Xiao, and Q. Zhang, Vertically aligned CNTs supported Ge thin film as high performance 3D anodes for lithium ion batteries. *Small*, under revision.

References

1. J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359-367.
2. B. Scrosati and J. Garche, *Journal of Power Sources*, 2010, **195**, 2419-2430.
3. B. A. Boukamp, G. C. Lesh and R. A. Huggins, *J Electrochem Soc*, 1981, **128**, 725-729.
4. U. Kasavajjula, C. Wang and A. J. Appleby, *Journal of Power Sources*, 2007, **163**, 1003-1039.
5. D. W. Murphy, F. J. Di Salvo, J. N. Carides and J. V. Waszczak, *Mater Res Bull*, 1978, **13**, 1395-1402.
6. B. J. Landi, M. J. Ganter, C. D. Cress, R. A. DiLeo and R. P. Raffaele, *Energy & Environmental Science*, 2009, **2**, 638-654.
7. J. B. Goodenough and Y. Kim, *Chemistry of Materials*, 2009, **22**, 587-603.
8. A. N. Dey, *J Electrochem Soc*, 1971, **118**, 1547-1549.
9. B. M. L. Rao, R. W. Francis and H. A. Christopher, *J Electrochem Soc*, 1977, **124**, 1490-1492.
10. W.-J. Zhang, *Journal of Power Sources*, 2011, **196**, 13-24.
11. D. Larcher, S. Beattie, M. Morcrette, K. Edstrom, J.-C. Jumas and J.-M. Tarascon, *Journal of Materials Chemistry*, 2007, **17**, 3759-3772.
12. Y.-N. Zhou, W.-J. Li, H.-J. Chen, C. Liu, L. Zhang and Z. Fu, *Electrochem Commun*, 2011, **13**, 546-549.
13. H. Ghassemi, M. Au, N. Chen, P. A. Heiden and R. S. Yassar, *Acs Nano*, 2011, **5**, 7805-7811.
14. M. N. Obrovac and L. Christensen, *Electrochemical and Solid-State Letters*, 2004, **7**, A93-A96.
15. T. D. Hatchard and J. R. Dahn, *J Electrochem Soc*, 2004, **151**, A838-A842.
16. M. J. Chon, V. A. Sethuraman, A. McCormick, V. Srinivasan and P. R. Guduru, *Phys Rev Lett*, 2011, **107**, 045503.
17. J. Saint, M. Morcrette, D. Larcher, L. Laffont, S. Beattie, J. P. Prs, D. Talaga, M. Couzi and J. M. Tarascon, *Adv Funct Mater*, 2007, **17**, 1765-1774.
18. J.-B. Kim, S.-H. Lim and S.-M. Lee, *J Electrochem Soc*, 2006, **153**, A455-A458.
19. N. Ding, J. Xu, Y. X. Yao, G. Wegner, X. Fang, C. H. Chen and I. Lieberwirth, *Solid State Ionics*, 2009, **180**, 222-225.
20. P. Yu, B. N. Popov, J. A. Ritter and R. E. White, *J Electrochem Soc*, 1999, **146**, 8-14.
21. A. Esmanski and G. A. Ozin, *Adv Funct Mater*, 2009, **19**, 1999-2010.
22. X. H. Liu, L. Q. Zhang, L. Zhong, Y. Liu, H. Zheng, J. W. Wang, J.-H. Cho, S. A. Dayeh, S. T. Picraux, J. P. Sullivan, S. X. Mao, Z. Z. Ye and J. Y. Huang, *Nano Lett*, 2011, **11**, 2251-2258.

23. Y. Yu, L. Gu, C. Zhu, S. Tsukimoto, P. A. van Aken and J. Maier, *Adv Mater*, 2010, **22**, 2247-2250.
24. V. A. Sethuraman, K. Kowolik and V. Srinivasan, *Journal of Power Sources*, 2011, **196**, 393-398.
25. M. N. Obrovac and L. J. Krause, *J Electrochem Soc*, 2007, **154**, A103-A108.
26. J. H. Ryu, J. W. Kim, Y.-E. Sung and S. M. Oh, *Electrochemical and Solid-State Letters*, 2004, **7**, A306-A309.
27. G. X. Wang, L. Sun, D. H. Bradhurst, S. Zhong, S. X. Dou and H. K. Liu, *Journal of Power Sources*, 2000, **88**, 278-281.
28. J. W. Kim, J. H. Ryu, K. T. Lee and S. M. Oh, *Journal of Power Sources*, 2005, **147**, 227-233.
29. I. s. Kim, P. N. Kumta and G. E. Blomgren, *Electrochemical and Solid-State Letters*, 2000, **3**, 493-496.
30. Z. P. Guo, Z. W. Zhao, H. K. Liu and S. X. Dou, *Journal of Power Sources*, 2005, **146**, 190-194.
31. A. Netz, R. A. Huggins and W. Weppner, *Journal of Power Sources*, 2003, **119–121**, 95-100.
32. J. Yang, Y. Takeda, N. Imanishi, C. Capiglia, J. Y. Xie and O. Yamamoto, *Solid State Ionics*, 2002, **152–153**, 125-129.
33. G. A. Roberts, E. J. Cairns and J. A. Reimer, *Journal of Power Sources*, 2002, **110**, 424-429.
34. S.-M. Hwang, H.-Y. Lee, S.-W. Jang, S.-M. Lee, S.-J. Lee, H.-K. Baik and J.-Y. Lee, *Electrochemical and Solid-State Letters*, 2001, **4**, A97-A100.
35. L. Y. Beaulieu, K. C. Hewitt, R. L. Turner, A. Bonakdarpour, A. A. Abdo, L. Christensen, K. W. Eberman, L. J. Krause and J. R. Dahn, *J Electrochem Soc*, 2003, **150**, A149-A156.
36. A. M. Wilson, G. Zank, K. Eguchi, W. Xing and J. R. Dahn, *Journal of Power Sources*, 1997, **68**, 195-200.
37. W.-R. Liu, J.-H. Wang, H.-C. Wu, D.-T. Shieh, M.-H. Yang and N.-L. Wu, *J Electrochem Soc*, 2005, **152**, A1719-A1725.
38. G. X. Wang, J. Yao and H. K. Liu, *Electrochemical and Solid-State Letters*, 2004, **7**, A250-A253.
39. Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano and Y. Takeda, *Electrochemical and Solid-State Letters*, 2004, **7**, A369-A372.
40. G. X. Wang, J. H. Ahn, J. Yao, S. Bewlay and H. K. Liu, *Electrochem Commun*, 2004, **6**, 689-692.
41. W.-R. Liu, M.-H. Yang, H.-C. Wu, S. M. Chiao and N.-L. Wu, *Electrochemical and Solid-State Letters*, 2005, **8**, A100-A103.
42. Z. Chen, L. Christensen and J. R. Dahn, *Electrochem Commun*, 2003, **5**, 919-923.
43. J. Li, R. B. Lewis and J. R. Dahn, *Electrochemical and Solid-State Letters*, 2007, **10**, A17-A20.

44. J. Li, D.-B. Le, P. P. Ferguson and J. R. Dahn, *Electrochimica Acta*, 2010, **55**, 2991-2995.
45. B. Lestriez, S. Bahri, I. Sandu, L. Roué and D. Guyomard, *Electrochem Commun*, 2007, **9**, 2801-2806.
46. N. S. Hochgatterer, M. R. Schweiger, S. Koller, P. R. Raimann, T. Wöhrle, C. Wurm and M. Winter, *Electrochemical and Solid-State Letters*, 2008, **11**, A76-A80.
47. J. R. Szczech and S. Jin, *Energy & Environmental Science*, 2011, **4**, 56-72.
48. S. Ohara, J. Suzuki, K. Sekine and T. Takamura, *Journal of Power Sources*, 2004, **136**, 303-306.
49. J. Li, A. K. Dozier, Y. Li, F. Yang and Y.-T. Cheng, *J Electrochem Soc*, 2011, **158**, A689-A694.
50. V. A. Sethuraman, V. Srinivasan, A. F. Bower and P. R. Guduru, *J Electrochem Soc*, 2010, **157**, A1253-A1261.
51. H.-C. Shin, J. A. Corno, J. L. Gole and M. Liu, *Journal of Power Sources*, 2005, **139**, 314-320.
52. M. Green, E. Fielder, B. Scrosati, M. Wachtler and J. S. Moreno, *Electrochemical and Solid-State Letters*, 2003, **6**, A75-A79.
53. K.-L. Lee, J.-Y. Jung, S.-W. Lee, H.-S. Moon and J.-W. Park, *Journal of Power Sources*, 2004, **129**, 270-274.
54. M. Uehara, J. Suzuki, K. Tamura, K. Sekine and T. Takamura, *Journal of Power Sources*, 2005, **146**, 441-444.
55. J.-B. Kim, H.-Y. Lee, K.-S. Lee, S.-H. Lim and S.-M. Lee, *Electrochem Commun*, 2003, **5**, 544-548.
56. R. A. Huggins and W. D. Nix, *Ionics*, 2000, **6**, 57-63.
57. K. E. Aifantis, S. A. Hackney and J. P. Dempsey, *Journal of Power Sources*, 2007, **165**, 874-879.
58. J. Christensen and J. Newman, *J Solid State Electrochem*, 2006, **10**, 293-319.
59. R. Deshpande, Y.-T. Cheng and M. W. Verbrugge, *Journal of Power Sources*, 2010, **195**, 5081-5088.
60. X. H. Liu, L. Zhong, S. Huang, S. X. Mao, T. Zhu and J. Y. Huang, *Acs Nano*, 2012, **6**, 1522-1531.
61. I. Ryu, J. W. Choi, Y. Cui and W. D. Nix, *Journal of the Mechanics and Physics of Solids*, 2011, **59**, 1717-1730.
62. C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins and Y. Cui, *Nat Nano*, 2008, **3**, 31-35.
63. H. T. Nguyen, F. Yao, M. R. Zamfir, C. Biswas, K. P. So, Y. H. Lee, S. M. Kim, S. N. Cha, J. M. Kim and D. Pribat, *Adv Energy Mater*, 2011, **1**, 1154-1161.
64. M. T. McDowell, S. Woo Lee, C. Wang and Y. Cui, *Nano Energy*, 2012, **1**, 401-410.

65. T. Song, J. Xia, J.-H. Lee, D. H. Lee, M.-S. Kwon, J.-M. Choi, J. Wu, S. K. Doo, H. Chang, W. I. Park, D. S. Zang, H. Kim, Y. Huang, K.-C. Hwang, J. A. Rogers and U. Paik, *Nano Lett*, 2010, **10**, 1710-1716.
66. M.-H. Park, M. G. Kim, J. Joo, K. Kim, J. Kim, S. Ahn, Y. Cui and J. Cho, *Nano Lett*, 2009, **9**, 3844-3847.
67. H. Kim, B. Han, J. Choo and J. Cho, *Angewandte Chemie*, 2008, **120**, 10305-10308.
68. Y.-C. Yen, S.-C. Chao, H.-C. Wu and N.-L. Wu, *J Electrochem Soc*, 2009, **156**, A95-A102.
69. L. Su, Z. Zhou and M. Ren, *Chemical Communications*, 2010, **46**, 2590-2592.
70. H. Jia, P. Gao, J. Yang, J. Wang, Y. Nuli and Z. Yang, *Adv Energy Mater*, 2011, **1**, 1036-1039.
71. F.-F. Cao, J.-W. Deng, S. Xin, H.-X. Ji, O. G. Schmidt, L.-J. Wan and Y.-G. Guo, *Adv Mater*, 2011, **23**, 4415-4420.
72. H. T. Nguyen, M. R. Zamfir, L. D. Duong, Y. H. Lee, P. Bondavalli and D. Pribat, *Journal of Materials Chemistry*, 2012, **22**, 24618-24626.
73. Y. Liu, N. S. Hudak, D. L. Huber, S. J. Limmer, J. P. Sullivan and J. Y. Huang, *Nano Lett*, 2011, **11**, 4188-4194.
74. N.-S. Choi, K. H. Yew, K. Y. Lee, M. Sung, H. Kim and S.-S. Kim, *Journal of Power Sources*, 2006, **161**, 1254-1259.
75. L. Chen, K. Wang, X. Xie and J. Xie, *Journal of Power Sources*, 2007, **174**, 538-543.
76. Y. Fan, K. Huang, Q. Zhang, Q. Xiao, X. Wang and X. Chen, *Journal of Materials Chemistry*, 2012, **22**, 20870-20873.
77. J. Bischof, D. Scherer, S. Herminghaus and P. Leiderer, *Phys Rev Lett*, 1996, **77**, 1536-1539.
78. D. Kim, A. L. Giermann and C. V. Thompson, *Applied Physics Letters*, 2009, **95**, 251903-251903.
79. Y. Zhang, Z.-W. Fu and Q.-Z. Qin, *Electrochem Commun*, 2004, **6**, 484-491.
80. A. A. Sirenko, J. R. Fox, I. A. Akimov, X. X. Xi, S. Ruvimov and Z. Liliental-Weber, *Solid State Communications*, 2000, **113**, 553-558.
81. X. H. Liu, H. Zheng, L. Zhong, S. Huang, K. Karki, L. Q. Zhang, Y. Liu, A. Kushima, W. T. Liang, J. W. Wang, J.-H. Cho, E. Epstein, S. A. Dayeh, S. T. Picraux, T. Zhu, J. Li, J. P. Sullivan, J. Cumings, C. Wang, S. X. Mao, Z. Z. Ye, S. Zhang and J. Y. Huang, *Nano Lett*, 2011, **11**, 3312-3318.
82. P. L. Taberna, S. Mitra, P. Poizot, P. Simon and J. M. Tarascon, *Nat Mater*, 2006, **5**, 567-573.
83. M. Nishizawa, K. Mukai, S. Kuwabata, C. R. Martin and H. Yoneyama, *J Electrochem Soc*, 1997, **144**, 1923-1927.
84. L.-F. Cui, R. Ruffo, C. K. Chan, H. Peng and Y. Cui, *Nano Lett*, 2008, **9**, 491-495.

85. L.-F. Cui, Y. Yang, C.-M. Hsu and Y. Cui, *Nano Lett*, 2009, **9**, 3370-3374.
86. H. Guan, X. Wang, S. Chen, Y. Bando and D. Golberg, *Chemical Communications*, 2011, **47**, 12098-12100.
87. X. Chen, K. Gerasopoulos, J. Guo, A. Brown, C. Wang, R. Ghodssi and J. N. Culver, *Acs Nano*, 2010, **4**, 5366-5372.
88. X. Fan, H. Zhang, N. Du, P. Wu, X. Xu, Y. Li and D. Yang, *Nanoscale*, 2012, **4**, 5343-5347.
89. K. Kang, K. Song, H. Heo, S. Yoo, G.-S. Kim, G. Lee, Y.-M. Kang and M.-H. Jo, *Chemical Science*, 2011, **2**, 1090-1093.
90. Y. Yao, K. Huo, L. Hu, N. Liu, J. J. Cha, M. T. McDowell, P. K. Chu and Y. Cui, *Acs Nano*, 2011, **5**, 8346-8351.
91. T. Takamura, S. Ohara, M. Uehara, J. Suzuki and K. Sekine, *Journal of Power Sources*, 2004, **129**, 96-100.
92. L. Hu, H. Wu, Y. Gao, A. Cao, H. Li, J. McDough, X. Xie, M. Zhou and Y. Cui, *Adv Energy Mater*, 2011, **1**, 523-527.
93. J. W. Wang, X. H. Liu, K. Zhao, A. Palmer, E. Patten, D. Burton, S. X. Mao, Z. Suo and J. Y. Huang, *Acs Nano*, 2012, **6**, 9158-9167.
94. N. Srivastava, R. V. Joshi and K. Banerjee, Electron Devices Meeting, 2005. IEDM Technical Digest. IEEE International, 2005.
95. Y. Fan, Q. Zhang, C. Lu, Q. Xiao, X. Wang and B. k. Tay, *Nanoscale*, 2013.
96. A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes and M. L. Simpson, *Journal of Applied Physics*, 2005, **97**, 041301.
97. P. E. Nolan, D. C. Lynch and A. H. Cutler, *The Journal of Physical Chemistry B*, 1998, **102**, 4165-4175.
98. C.-M. Wang, X. Li, Z. Wang, W. Xu, J. Liu, F. Gao, L. Kovarik, J.-G. Zhang, J. Howe, D. J. Burton, Z. Liu, X. Xiao, S. Thevuthasan and D. R. Baer, *Nano Lett*, 2012, **12**, 1624-1632.
99. K. Bhattacharya and D. Das, *Nanotechnology*, 2007, **18**.
100. A. Gajović, D. Gracin, I. Djerdj, N. Tomašić, K. Jurać and D. S. Su, *Applied Surface Science*, 2008, **254**, 2748-2754.
101. H. Ma, F. Cheng, J. Y. Chen, J. Z. Zhao, C. S. Li, Z. L. Tao and J. Liang, *Adv Mater*, 2007, **19**, 4067-4070.
102. E. Pollak, G. Salitra, V. Baranchugov and D. Aurbach, *The Journal of Physical Chemistry C*, 2007, **111**, 11437-11444.
103. J. P. Maranchi, A. F. Hepp and P. N. Kumta, *Electrochemical and Solid-State Letters*, 2003, **6**, A198-A201.
104. S. Ohara, J. Suzuki, K. Sekine and T. Takamura, *Journal of Power Sources*, 2003, **119-121**, 591-596.
105. H. Guo, H. Zhao, C. Yin and W. Qiu, *Materials Science and Engineering: B*, 2006, **131**, 173-176.
106. M. K. Datta, J. Maranchi, S. J. Chung, R. Epur, K. Kadakia, P. Jampani and P. N. Kumta, *Electrochimica Acta*, 2011, **56**, 4717-4723.

107. H. Wu, G. Chan, J. W. Choi, I. Ryu, Y. Yao, M. T. McDowell, S. W. Lee, A. Jackson, Y. Yang, L. Hu and Y. Cui, *Nat Nano*, 2012, **7**, 310-315.
108. Y. Fan, Q. Zhang, Q. Xiao, X. Wang and K. Huang, *Carbon*, 2013, **59**, 264-269.
109. K. Q. Peng and S. T. Lee, *Adv Mater*, 2011, **23**, 198-215.
110. T. Song, S.-T. Lee and B. Sun, *Nano Energy*, 2012, **1**, 654-673.
111. A. I. Hochbaum, R. Fan, R. He and P. Yang, *Nano Lett*, 2005, **5**, 457-460.
112. K. Q. Peng, Y. J. Yan, S. P. Gao and J. Zhu, *Adv Mater*, 2002, **14**, 1164-1167.
113. Z. P. Huang, N. Geyer, P. Werner, J. de Boor and U. Gosele, *Adv Mater*, 2011, **23**, 285-308.
114. H. A. Chen, H. Wang, X. H. Zhang, C. S. Lee and S. T. Lee, *Nano Lett*, 2010, **10**, 864-868.
115. K. Q. Peng, J. S. Jie, W. J. Zhang and S. T. Lee, *Applied Physics Letters*, 2008, **93**.
116. R. Huang, X. Fan, W. C. Shen and J. Zhu, *Applied Physics Letters*, 2009, **95**.
117. M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis and H. A. Atwater, *Nat Mater*, 2010, **9**, 239-244.
118. W. K. Choi, T. H. Liew, M. K. Dawood, H. I. Smith, C. V. Thompson and M. H. Hong, *Nano Lett*, 2008, **8**, 3799-3802.
119. Z. Huang, H. Fang and J. Zhu, *Adv Mater*, 2007, **19**, 744-748.
120. K. Peng, M. Zhang, A. Lu, N.-B. Wong, R. Zhang and S.-T. Lee, *Applied Physics Letters*, 2007, **90**, 163123-163123.
121. Z. Huang, X. Zhang, M. Reiche, L. Liu, W. Lee, T. Shimizu, S. Senz and U. Gösele, *Nano Lett*, 2008, **8**, 3046-3051.
122. C.-M. Hsu, S. T. Connor, M. X. Tang and Y. Cui, *Applied Physics Letters*, 2008, **93**, 133109-133103.
123. Z. Huang, T. Shimizu, S. Senz, Z. Zhang, X. Zhang, W. Lee, N. Geyer and U. Gösele, *Nano Lett*, 2009, **9**, 2519-2525.
124. J. Kim, H. Han, Y. H. Kim, S.-H. Choi, J.-C. Kim and W. Lee, *Acs Nano*, 2011, **5**, 3222-3229.