The Pennsylvania State University

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MULTISCALE CHEMO-MECHANICAL MECHANICS OF HIGH-CAPACITY ANODE MATERIALS IN LITHIUM-ION NANO-BATTERIES

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Hui Yang

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The dissertation of Hui Yang was reviewed and approved* by the following:

Sulin Zhang Associate Professor of Engineering Science and Mechanics Dissertation Advisor Chair of Committee

Charles E. Bakis Distinguished Professor of Engineering Science and Mechanics

Long-Qing Chen Distinguished Professor of Materials Science and Engineering and Engineering Science and Mechanics

Adri C.T. van Duin Associate Professor of Mechanical and Nuclear Engineering

Judith A. Todd Professor of Engineering Science and Mechanics P.B. Breneman Department Head Department of Engineering Science and Mechanics

*Signatures are on file in the Graduate School

ABSTRACT

Rechargeable lithium-ion batteries (LIBs), which are the most prevailing and promising electrochemical energy storage and conversion devices due to their high energy density and design flexibility, are widely used in portable electronics and electric vehicles. Currently commercialized LIBs adopt graphite as anode for its long cycle life, abundant material supply, and relatively low cost. However, graphite suffers low specific charge capacity (372 mAhg^{-1}) , which is obviously insufficient for powering new generation electronic devices. Thus, considerable efforts are being undertaking to develop alternative anode materials with low cost, high capacity, and long cycle life. A variety of high capacity anode materials have been identified, and silicon (Si) stands as the leading candidate and has attracted much attention for its highest theoretical capacity (4200 mAhg⁻¹). Nevertheless, inherent to the high-capacity electrodes, lithium (Li) insertionextraction cycling induces huge volumetric expansion and stress inside the electrodes, leading to fracture, pulverization, electrical disconnectivity, and ultimately huge capacity loss. Therefore, a fundamental understanding of the degradation mechanisms in the highcapacity anodes during lithiation-delithiation cycling is crucial for the rational design of next-generation failure-resistant electrodes.

In this thesis, a finite-strain chemo-mechanical model is formulated to study the lithiation-induced phase transformation, morphological evolution, stress generation and fracture in high capacity anode materials such as Si and germanium (Ge). The model couples Li reaction-diffusion with large elasto-plastic deformation in a bidirectional manner: insertion of the Li into electrode generates localized stress, which in turn mediates electrochemical insertion rates. Several key features observed from recent transmission electron microscopy (TEM) studies are incorporated into the modeling framework, including the sharp interface between the lithiated amorphous shell and unlithiated crystalline core, crystallographic orientation-dependent electrochemical reaction rate, and large-strain plasticity. The simulation results demonstrate that the model faithfully predicts the anisotropic swelling of lithiated crystalline silicon nanowires (*c*-SiNWs) observed from previous experimental studies. Stress analysis reveals that the SiNWs are prone to surface fracture at the angular sites where two adjacent {110} facets intersect, consistent with previous experimental observations. In addition, Li insertion can induce high hydrostatic pressure at and closely behind the reaction front, which can lead to the lithiation retardation observed by TEM studies.

For a comparative study, the highly reversible expansion and contraction of crystalline germanium nanoparticles (c-GeNPs) under lithiation-delithiation cycling are reported. During multiple cycles to the full capacity, the GeNPs remain robust without any visible cracking despite ~260% volume changes, in contrast to the size dependent fracture of crystalline silicon nanoparticles (c-SiNPs) upon the first lithiation. The comparative study of c-SiNPs, c-GeNPs, and amorphous SiNPs (a-SiNPs) through *in-situ* TEM and chemo-mechanical modeling suggest that the tough behavior of c-GeNPs and a-SiNPs can be attributed to the weak lithiation anisotropy at the reaction front. In the absence of lithiation anisotropy, the c-GeNPs and a-SiNPs experience uniform hoop tension in the surface layer without the localized high stress and therefore remain robust

throughout multicycling. In addition, the two-step lithiation in *a*-SiNPs can further alleviate the abruptness of the interface and hence the incompatible stress at the interface, leading to an even tougher behavior of *a*-SiNPs. Therefore, eliminating the lithiation anisotropy presents a novel pathway to mitigate the mechanical degradation in high-capacity electrode materials.

In addition to the study of the retardation effect caused by lithiation self-generated internal stress, the influence of the external bending on the lithiation kinetics and deformation morphologies in germanium nanowires (GeNWs) is also investigated. Contrary to the symmetric core-shell lithiation in free-standing GeNWs, bending a GeNW during lithiation breaks the lithiation symmetry, speeding up lithiation at the tensile side while slowing down at the compressive side of the GeNWs. The chemomechanical modeling further corroborates the experimental observations and suggests the stress dependence of both Li diffusion and interfacial reaction rate during lithiation. The finding that external load can mediate lithiation kinetics opens new pathways to improve the performance of electrode materials by tailoring lithiation rate via strain engineering. Furthermore, in the light of bending-induced symmetry breaking of lithiation, the mechanically controlled flux of the secondary species (i.e., Li) features a novel energy harvesting mechanism through mechanical stress.

Besides the continuum level chemo-mechanical modelings, molecular dynamics simulations with the ReaxFF reactive force field are also conducted to investigate the fracture mechanisms of lithiated graphene. The simulation results reveal that Li diffusion toward the crack tip is both energetically and kinetically favored owing to the crack-tip stress gradient. The stress-driven Li diffusion results in Li aggregation around the crack tip, chemically weakening the crack-tip bond and at the same time causing stress relaxation. As a dominant factor in lithiated graphene, the chemical weakening effect manifests a self-weakening mechanism that causes the fracture of the graphene.

Moreover, lithiation-induced fracture mechanisms of defective single-walled carbon nanotubes (SWCNTs) are elucidated by molecular dynamics simulations. The variation of defect size and Li concentration sets two distinct fracture modes of the SWCNTs upon uniaxial stretch: abrupt and retarded fracture. Abrupt fracture either involves spontaneous Li weakening of the propagating crack tip or is absent of Li participation, while retarded fracture features a "wait-and-go" crack extension process in which the crack tip periodically arrests and waits to be weakened by diffusing Li before extension resumes. The failure analysis of the defective CNTs upon lithiation, together with the cracked graphene, provides fundamental guidance to the lifetime extension of high capacity anode materials.

TABLE OF CONTENTS

LIST OF FIGURES	ix
LIST OF TABLES	XV
ACKNOWLEDGEMENTS	xvi
Chapter 1 Introduction	1
1.1 Motivation	1
1.2 Background	3
1.2.1 The Working Principle of Lithium-Ion Batteries	3
1.2.2 Mechanical Degradation of High-Capacity Electrodes	7
1.2.3 Chemo-Mechanics in Electrode Degradation	11
1.3 Scope of the Thesis	15
Chapter 2 A Chemo-Mechanical Model of Lithiation in Silicon	18
2.1 Introduction	18
2.2 Key Physical Features in Lithiation of Crystalline Silicon	21
2.2.1 Sharp Phase Boundary	21
2.2.2 Time Scales of Reaction and Diffusion	22
2.2.3 Lithiation Anisotropy	23
2.2.4 Lithiation-Induced Large Deformation	25
2.3 A Chemo-Mechanical Model	
2.3.1 Evolving the Two-Phase Microstructure	
2.3.2 Lithiation-Induced Elasto-Plastic Deformation	
2.3.3 Boundary Value Problem	
2.4 Numerical Implementation	
2.4.1 Model Parameters	
2.4.2 Treatment of the Interfacial Domain	
2.5 Numerical Results	
2.5.1 Lithiation-Induced Anisotropic Swelling: Small Strain Model	
2.5.2 Lithiation-Induced Anisotropic Swelling: Finite-Strain Model	
2.6 Discussions	44
2.7 Conclusions	47
Chapter 3 Tough Germanium Nanoparticles under Electrochemical Cycling	50
3.1 Introduction	50
3.2 Experimental Methodology	
3.3 Results and Discussion	
3.3.1 Experimental Results	
3.3.2 Numerical Results	
3.4 Conclusions	65

	4.1 Introduction	6
	4.2 Experimental Methodology	6
	4.3 Results and Discussion.	7
	4.3.1 Experimental Results	7
	4.3.2 Numerical Results	7
	4.4 Conclusions	8
Cha	apter 5 Self-Weakening in Lithiated Graphene Electrodes	8
	5.1 Introduction	8
	5.2 Methodology	8
	5.3 Results and Discussion	9
	5.3.1 Li Stability on a Cracked Graphene	9
	5.3.2 Migration Pathways and Kinetic Barriers of Li on a Cracked Graphene.	9
	5.3.3 Chemical Weakening and Crack-Tip Stress Relaxation	9
	5.4 Conclusions	9
Cha	apter 6 Lithiation-Induced Corrosive Fracture in Defective Carbon Nanotubes	9
	6.1 Introduction	9
	6.2 Methodology	1
	6.3 Results and Discussion	1
	6.4 Conclusions	1
Cha	apter 7 Conclusions and Future Work	1
	7.1 Conclusions	1
	7.2 Future Work	1

viii

LIST OF FIGURES

Figure 1-1. Comparison of the different types of batteries in terms of volumetric and gravimetric energy density [1]. Lithium-ion batteries (LIBs) are the most prevailing and promising devices for electrochemical energy storage and conversion due to their high energy density and design flexibility
Figure 1-2. Schematic of a lithium-ion battery comprised of a negative electrode (graphite) and a positive electrode (LiCoO ₂), separated by a non-aqueous liquid electrolyte. Li ions move from the negative (positive) electrode to the positive (negative) electrode through the electrolyte during discharging (charging); meanwhile electrons move through an external circuit to maintain the electrical neutrality. Solid electrolyte interfaces (SEIs) are formed during the electrochemical cycling. Current collectors (here are Al and Cu) are used to transport electrons to and from the electrodes [22].
Figure 1-3. Diagram illustrating the lithium ion (Li ⁺) capacity and electrochemical potential with respect to lithium (Li) metal for conventional anode (red axis) and cathode (blue axis) materials. The battery potential is the relative difference between the voltage of the selected positive electrode materials (blue ovals) and voltage of the corresponding negative electrode material (red ovals) [22]
Figure 1-4. Gravimetric capacities of different candidate anode materials. Capacity of graphite (C) is given as a reference. Silicon (Si) stands as the leading candidate for the highest capacity
Figure 1-5. Mechanical degradation of Si electrodes: (a) Schematic and (b) experiment of morphological changes that occur in Si thin films during electrochemical cycling [14]. The volume of Si anodes changes by about 300% during cycling. As a result, Si films tend to pulverize. Much of the material loses contact with the current collector, causing the capacity fading
Figure 1-6. Schematic (a) and experiment (b) of electrochemical cycling of Si nanowires (SiNWs) grown on the current collector [27]. Facile strain relaxation in the Si nanowires allows them to increase in diameter and length without breaking. During the first cycle, the initial crystalline wires are transformed into amorphous Li _x Si with embedded nanocrystalline Si. The direct connection between Si nanowires (SiNWs) and current collector facilitates efficient 1D electron transport along the SiNWs9
Figure 2-1. SEM [20] and TEM [19] images of anisotropic swelling and fracture in lithiated SiNWs with four different axial orientations: (a) <100>, (b) <110>, (c) <111>, and (d) <112>. Top: Cracks oriented along the axes of the SiNWs are indicated by red arrows. Bottom: The corresponding crystallographic orientations of the facets on the sidewalls of each SiNW are shown. The scale bars in the insets are

Figure 2-2. <i>In-situ</i> TEM experiment of lithiation of a $<112>c$ -SiNW. (a) TEM image of a <i>c</i> -SiNW prior to lithiation. (b) Formation of a core-shell structure in a partially lithiated SiNW, where the crystalline core (<i>c</i> -Si) is surrounded by the amorphous shell (<i>a</i> -Li _x Si). A thin layer of Li ₂ O is formed on the outer surface of the lithiated shell. (c) The amorphous-crystalline interface (ACI), i.e., the phase boundary separating the amorphous lithiated shell and the unlithiated crystalline core, is atomically sharp (~1 nm) [55]
Figure 2-3. Decomposition of a partially lithiated core-shell structure into three sub- domains: two bulk domains, one behind the reaction front ($c \ge c_+$, red region) and
the other in front of the reaction front ($c < c_{-}$, blue region), and the amorphous- crystalline interfacial domain ($c_{-} < c < c_{+}$) with thickness δ between the two bulk domains, where c is the Li concentration normalized by that of the fully lithiated phase of Li ₁₅ Si ₄ , with $c = 1$ representing the amorphous Li ₁₅ Si ₄ (red region) and $c = 0$ pure crystalline Si (blue region)
Figure 2-4. Orientation-dependent diffusion constant (modeling the lithiation reaction rate) at the sharp amorphous-crystalline interface (ACI) on the cross sections of SiNWs with different axial orientations: <100>, <110>, <111>, and <112>29
Figure 2-5. 3D morphologies of the lithiated SiNWs of different axial crystallographic orientations: (a) <100>; (b) <110>; (c) <111>; and (d) <112>. The Li concentrations on the surface and different cross sections are indicated by the contours. Transition colors from red to blue indicate the reaction fronts. In each SiNW, a quarter of the partially lithiated cross section (shaded) is highlighted by an enlarged image with finite element meshes attached, showing that the width of the simulated interface is only a few elements
Figure 2-6. Li flux profiles at a representative lithiation snapshot ($t = 0.3$) for all the four SiNWs, showing that the dominant flux in the <110> directions, a direct consequence of high reactivity of Li at the {110} phase boundary
Figure 2-7. Maximum principal Cauchy stress distributions (based on small-strain theory) in the lithiated SiNWs (from left to right: <100>, <110>, <111>, and <112>) at the lithiation snapshots $t = 0.3$, where t is normalized time
Figure 2-8. Maximum principal Cauchy stress distributions (based on finite-strain theory) in the lithiated SiNWs (from left to right: $<100>$, $<110>$, $<111>$, and $<112>$) at the lithiation snapshots $t = 0.3$, where t is normalized time
Figure 2-9. Stress contours (the maximal principal Cauchy stress) in the lithiated SiNWs. From left to right, the four columns represent the morphological changes and stress distribution in <100>, <110>, <111>, and <112> SiNWs, respectively. Each column includes four simulation snapshots ($t = 0.015$, 0.05, 0.2 and 0.3, where t is the normalized time) of the SiNWs being lithiated

xi

- Figure 3-5. Chemo-mechanical modeling of the core-shell structure and stress generation in the cross section of a lithiated nanowire, showing the effect of the lithiation anisotropy. (a1) Orientation-dependent interfacial reaction rate in <111> *c*-SiNW leads to a hexagonal shaped reaction front in the cross section of the nanowire, represented by the transition colors from red to blue. (b1, c1) Isotropic interfacial reaction rate results in circular shaped reaction fronts in the cross sections of *c*-GeNW and *a*-SiNW. Li concentration in (a1) and (c1) is normalized by that of Li₁₅Si₄, while the one in (b1) is normalized by that of Li₁₅Ge₄. (a2, b2, c2) Hoop stress (σ_{θ}) profiles in cross sections of <111> *c*-Si (a2), *c*-Ge (b2), and *a*-Si (c2) nanowires. Lithiation anisotropy causes the intensified hoop tension at the angular sites between two {110} adjacent facets in the <111> *c*-SiNW (a2), while such intensified tension is absent in the other two nanowires (b2 and c2).................64

- Figure 4-4. Simulation setup of a GeNW under lithiation. (a) Solid model used in the simulation, consisting of a rigid substrate representing the counter electrode and a

- Figure 4-5. 3D chemo-mechanical modeling of the lithiation kinetics and stress generation in a GeNW subject to bending. (a1-a5) The Li concentration profiles at different lithiation stages; (b1-b5) The corresponding hydrostatic stress concentration profiles. The symmetry breaking in lithiation is clearly shown by both the longitudinal and cross-sectional views of the Li concentration and stress profiles.
 (c) Lithiation kinetics of the simulated GeNW. The lithiation thickness is normalized by the diameter of the simulated GeNW, and the time is normalized by the total time for the cross section to be fully lithiated.
- Figure 5-2. Stress-mediated stability of Li adatom. (a) The pressure profile at the crack tip obtained from continuum fracture mechanics ($P \propto \cos(\theta/2)$); (b) Virial stress profile at the crack tip; (c) the stability map. From green to red colors the stability of the Li adatom increases. The high-stability domain at the crack tip is inconsistent with the high-pressure contour in (a) and (b), suggesting that shear stress and possibly the free crack edges play additional roles in the stability of the Li adatom......90
- Figure 5-4. Load dependent migration barrier of the Li adatom ($\theta = 0^{\circ}$). As the applied load (stress intensity factor $\hat{K}_{I} = K_{I}/2\mu$) increases, the migration barrier decreases...94
- Figure 6-1. Fracture of defective (18, 0) SWCNTs with varying lithium (Li) concentrations. The green dots represent carbon atoms, while the purple dots represent Li. The applied tensile strains are indicated. (A) The SWCNT with a hole-like defect formed by removing 10 carbon atoms. Prior to crack propagation, Li

aggregates to the hole. During crack propagation, Li flows to the newly cracked surface and crack tip, dynamically weakening the crack and modulating the crack propagation. The SWCNT with different Li concentrations breaks at different fracture strains. (B) SWCNT with a single vacancy defect. Fracture occurs abruptly for all the cases, and Li diffusion plays an insignificant role once the crack is initiated. Except for the Li-free case, for all the other cases with different Li concentrations the SWCNT breaks at approximately the same fracture strain......103

Figure 6-2. (a) Stress-strain curve of the SWCNTs containing a hole-like defect with different Li densities under tensile loading. (b) Three fractural states of SWCNTs showing a "wait-and-go" fracture behavior of SWCNTs with a low Li density (Li:C -1.12)	104
- 1.12)	104
Figure 6-3. Stress-strain curves of the SWCNTs containing a vacancy defect with different Li densities under tensile loading	106
Figure 6-4. Active lithium (Li) diffusion on the surface of SWCNTs with a hole-like (a) and single-vacancy defect (b). For both (a) and (b), Li:C = 1:12.	107
Figure 6-5. Loading rate effect on the lithiation-induced weakening of SWCNTs.	109

LIST OF TABLES

Table 6-1. The onset fracture strain, rapture strain, and fracture strength of defective (18,0) SWCNTs with varying Li concentrations (SV: single vacancy).105

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Chapter 1

Introduction

1.1 Motivation

The exponential growth in the demands for electrical energy storage, not only for portable electronic devices, such as cellular phones and laptop computers, but also for transportation, load-leveling, and commercialization of renewable resources such as solar and wind power, has attracted enormous interest in compact, light-weight, and highcapacity batteries that can offer high energy densities, as batteries are by far the most common form of storing electrical energy [1-4]. Therefore, advanced battery technologies are critically important for the wide range applications of various batteries, from portable electronics to electric vehicles [5-8].

Among the present battery technologies, rechargeable lithium-ion batteries (LIBs), which are the most prevailing and promising devices for electrochemical energy storage and conversion due to their high energy density and design flexibility [1, 2, 6, 8-10], as shown in Fig. 1-1, are widely used in portable electronics and electric vehicles. Currently commercialized LIBs adopt graphite as anode for its long cycle life, abundant material supply, and relatively low cost. However, graphite suffers low specific charge capacity (372 mAhg⁻¹) [11, 12], which is obviously insufficient for powering new-generation electronic devices. Thus, alternative anode materials with low cost, high capacity, and long cycle life need to be developed.



Figure 1-1. Comparison of the different types of batteries in terms of volumetric and gravimetric energy density [1]. Lithium-ion batteries (LIBs) are the most prevailing and promising devices for electrochemical energy storage and conversion due to their high energy density and design flexibility.

A variety of high capacity anode materials have been identified, and silicon (Si) stands as the leading candidate and has attracted much attention for its highest theoretical capacity (4200 mAhg⁻¹) [9, 11-13]. Nevertheless, during electrochemical lithiation-delithiation process, all these high capacity anode materials inherently experiences large volume change (especially up to 300% for Si), leading to fracture, pulverization, electrical disconnectivity, and ultimately huge capacity loss [12, 14-20]. Therefore, a fundamental understanding of the degradation mechanisms in the pertinent anode materials during lithiation-delithiation cycling is crucial for the rational design of high energy density anodes in LIBs.

1.2 Background

A battery is an energy storage device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical reaction [21]. For a rechargeable battery, the process can be reversed during the charging period. Among the various existing technologies, LIBs are the best performing ones owing to their high energy density [1, 2, 6, 8-10], which exceeds any competing technologies by at least a factor of 2.5 [1].

1.2.1 The Working Principle of Lithium-Ion Batteries

A battery contains one or more electrochemical cells that are connected in series and/or in parallel to provide the desired output voltage and capacity, respectively [1, 3, 21]. Each cell consists of three major components: negative electrode (anode), positive electrode (cathode), and electrolyte which separates the two electrodes, as shown in Fig. 1-2 [22]. The electrolyte must have good ionic conductivity but not be electronically conductive in order to provide the medium for the transfer of lithium ions (Li⁺) but not electrons between the anode and cathode. Additionally, current collectors, which are usually metals and must not react with the electrodes materials, are used to allow the transport of electrons to and from the electrodes. Typically, copper (Cu) is used for the anode and aluminum (Al) for the cathode. As LIBs are based on the electrochemical reaction during which Li is inserted into or extracted from both cathode (positive electrode) and anode (negative electrode), when the battery is being charged, the electrochemical potential difference of Li⁺ in the two electrodes acts as a driving force for the migration of Li⁺ from the cathode to the anode through the electrolyte. Meanwhile, electrons flow from the cathode to the anode through the external circuit connected to the two current collectors. Such process will be reversed during discharging period, and the electrical energy transformed from the chemical energy stored in the electrodes will be used to power the external working load.



Figure 1-2. Schematic of a lithium-ion battery comprised of a negative electrode (graphite) and a positive electrode ($LiCoO_2$), separated by a non-aqueous liquid electrolyte. Li ions move from the negative (positive) electrode to the positive (negative) electrode through the electrolyte during discharging (charging); meanwhile electrons move through an external circuit to maintain the electrical neutrality. Solid electrolyte interfaces (SEIs) are formed during the electrochemical cycling. Current collectors (here are Al and Cu) are used to transport electrons to and from the electrodes [22].

Once the positive and negative electrodes are connected externally, the electrochemical reactions proceed simultaneously at both electrodes, thereby liberating

electrons and enabling the current to go through the external circuit to do work. The measures of the performance of a battery, such as cell potential, capacity, and energy density which are determined by the product of cell capacity and potential, are related to the intrinsic properties of the chosen anode and cathode materials. Energy density, the amount of electrical energy that a battery can deliver, is a function of the cell potential (V_{oc}) and capacity (Ahkg⁻¹), and can be expressed either per unit of weight (gravimetric energy density, Whkg⁻¹) or per unit of volume (volumetric energy density, Whl⁻¹) [1]. Both of the cell potential and capacity are directly linked to the chemistry of the system. The cell potential V_{oc} of a lithium (Li) cell can be determined by the difference in the Li chemical potential between the cathode $\mu_{Li(c)}$ and the anode $\mu_{Li(a)}$ as:

$$V_{oc} = \frac{\mu_{Li(c)} - \mu_{Li(a)}}{F}$$
(1-1)

where, F is the Faraday constant. The theoretical capacity of a cell, expressed as the total quantity of electricity involved in the electrochemical reaction, is also determined by the amount of active materials in the cell [21]. Figure 1-3 shows all the conventional anode and cathode materials with their Li⁺ capacity and electrochemical potential compared with Li metal [22]. In addition, the nature of the interface between the cell electrodes and electrolyte determines the cycle life of a battery, and safety is a function of the stability of the electrode materials and interfaces [1]. Therefore, the construction of high-performance batteries requires a careful selection of existing and new materials as negative and positive electrodes, as well as appropriate electrolyte, in order to minimize detrimental reactions associated with the electrode-electrolyte interface [1].



Figure 1-3. Diagram illustrating the lithium ion (Li⁺) capacity and electrochemical potential with respect to lithium (Li) metal for conventional anode (red axis) and cathode (blue axis) materials. The battery potential is the relative difference between the voltage of the selected positive electrode materials (blue ovals) and voltage of the corresponding negative electrode material (red ovals) [22].

According to the working principle of LIBs, the capacity of the LIBs largely depends on the ability of the electrodes to accommodate Li atoms [6]. For this reason, significant research over the last decade has been directed towards searching for materials with high capacity to increase battery efficiency. Graphitized carbon, the most commonly used anode for LIBs, exhibits relatively small volumetric change, stable working voltage and good cycle performance. However, the chemical compound LiC_{6} limits the

theoretical capacity of Li-C anodes to 372 mAhg⁻¹ [11, 12], which is insufficient for high power applications. Compared to the Li-C anodes, a variety of Li-alloy (Li_xM, M = Sn, Al, Ge, Si) anodes show substantially higher theoretical capacity and high Li packing density, as shown in Fig. 1-4 [11, 12, 23]. Si, as the leading candidate for anode material in LIBs, has a theoretical capacity of 4200 mAhg⁻¹ with the formation of Li₂₂Si₅ alloy [9, 11-13], one order of magnitude higher than graphitized carbon.



Figure 1-4. Gravimetric capacities of different candidate anode materials. Capacity of graphite (C) is given as a reference. Silicon (Si) stands as the leading candidate for the highest capacity.

1.2.2 Mechanical Degradation of High-Capacity Electrodes

Inherent to the high-capacity electrodes, Li insertion-extraction cycling induces huge volumetric expansion and stress inside the electrodes, causing fast disintegration or cracking [12, 14-20, 24-26]. For instance, fully lithiated Si undergoes about 300% volume expansion [19]. The issue is even severer when an electrode undergoes high-rate charging or discharging, which is highly desired but often induces non-uniform Li

distribution in the electrode. The resulting large incompatible deformation between areas of different Li contents tends to initiate fracture, as shown in Fig. 1-5 [14], leading to the electro-chemo-mechanical failures of the electrodes. As exposed to the electrolyte through the newly cracked surfaces, the active material in the electrodes will react with the electrolyte to form solid electrolyte interfaces (SEI) on the newly cracked surfaces, resulting in the consumption of the active material in the electrodes and subsequent capacity fading of the battery. In addition, the mechanical degradation can also cause the loss of electrical contact between active materials, current collectors, and electrolytes, leading to poor cyclability.



Figure 1-5. Mechanical degradation of Si electrodes: (a) Schematic and (b) experiment of morphological changes that occur in Si thin films during electrochemical cycling [14]. The volume of Si anodes changes by about 300% during cycling. As a result, Si films tend to pulverize. Much of the material loses contact with the current collector, causing the capacity fading.

The inherent mechanical degradation of the high-capacity electrode materials directed researchers to seek for solutions from nanotechnology. During the last decade, the advance of nanotechnology enabled low-cost, fast fabrication of nanostructured materials with nanoscale controls on the size, shape, and chemical compositions. The development of nanostructured electrodes, on one hand, can provide facile strain relaxation, to some extent, to prevent electrode pulverization and maintain effective electrical contact between active material and the current collector, as shown in Fig. 1-6. It has been demonstrated that reduction of a particle size to nanoscale can change the crystal structure and modify the mechanism of volumetric expansion upon lithiation [27, 28]. On the other hand, the reduced dimensions can significantly increase the insertion-extraction rates of Li and, hence, facilitate high power capacity [10, 29]. The size effect has been explored in a variety of Si nanostructures [30-32]. Nanoelectrodes of different geometrical shapes were also considered, including nanowires (NWs) [18, 27, 28, 33-35], nanotubes [36-38], thin films [16, 39, 40], and nanoparticles (NPs) [41-44]. Another route to enhance the performance of electrodes is through composite design, where one material component (e.g., Si) contributes to the capacity of the electrode, while the other (e.g., carbon) to the conductivity and/or mechanical stability [45-54].



Figure 1-6. Schematic (a) and experiment (b) of electrochemical cycling of Si nanowires (SiNWs) grown on the current collector [27]. Facile strain relaxation in the Si nanowires allows them to increase in diameter and length without breaking. During the first cycle, the initial crystalline wires are transformed into amorphous Li_x Si with embedded nanocrystalline Si. The direct connection between Si nanowires (SiNWs) and current collector facilitates efficient 1D electron transport along the SiNWs.

In general, the nanostructured and nanocomposite electrodes indeed exhibited better capacity retention as compared to their bulk counterparts during electrochemical cycling. However, mechanical degradation remains a serious roadblock to the development of failure-resistant electrodes. In order to real-timely study the degradation of electrode at nanoscale, new experimental platform was developed recently. In the experiment, a nanoscale battery, in which the electrodes are comprised of nanoparticle or nanowire arrays, or even single nanoparticles and nanowires [19, 33, 35, 44, 55-60], is assembled. An high-resolution transmission electron microscope (TEM) is adopted to monitor the electrochemical cycling responses of the nano-battery. Such experimental setup allows real-time tracking of the tempo-spatial evolution of deformation, crack nucleation and propagation, and phase transformation during Li insertion-extraction cycling, thereby offering a unique platform for the study of degradation mechanisms in electrodes. A variety of high capacity anode materials have been investigated using the in-situ TEM combined with other techniques, i.e. ex-situ TEM and scanning electron microscope (SEM) [19, 20, 33, 35, 38, 44, 55-60]. Recent experimental results show that lithiation can drastically embrittle multi-walled carbon nanotubes (MWCNTs) [38], in opposite contrast to the highly reversible deformability of pristine CNTs. However, graphene is demonstrated as a robust anode material [56]. TEM studies also reveal that the crystallographic orientations of Si nanostructures significantly affect the anisotropic swelling of the structure after Li insertion, leading to the orientation- and size-dependent fracture patterns [18-20, 30, 57]. On the contrary, germanium (Ge), a group IV element as carbon and Si, undergoes nearly isotropic lithiation without fracture as well as amorphous Si [44, 57, 61]. In addition, core-shell composite designs are proved to not

only enhance the ability of the electrode for capacity retention, but also tailor the lithiation behavior by control the Li transport-insertion paths [52, 54, 62]. Despite the significant advances achieved through the *in-situ* TEM experiments, the fundamental understandings of the electro-chemo-mechanical processes with Li insertion and extraction at nanoscale are critically lacking. Particularly, the mechanisms of the electro-chemically induced mechanical failures of different anode materials, which can be serious handicaps for the further advances of high-capacity LIB techniques, are still uncovered.

1.2.3 Chemo-Mechanics in Electrode Degradation

Central to the electrode degradation are processes that couple the electrochemistry and large deformation mechanics in solid-state electrodes. A fundamental understanding of the processes is the prerequisite for a robust design of failure-resistant electrodes. During electrochemical cycling, the electrode materials may undergo a series of complex phase transformations [63, 64]. For example, the electrochemical reaction between Li and Si crystal yields solid-state amorphous phases at low temperature, but crystalline phases at high temperature (~415 °C) [63]. At the lithiation front, Li reacts with electrode materials. The mobility of the reaction front is determined by the reaction rate, which is demonstrated to be crystallographic orientation dependent [18, 19, 24, 44, 65]. Behind the lithiation front, the Li concentration gradient drives the Li diffusion. The reaction front mobility, diffusivity, and the mechanical properties of lithiated electrode materials are all phase (i.e., Li-concentration) dependent. In addition, the lithiation front separates the lithiated region from non-lithiated region, where incompatible strain and stress are generated [44, 55, 66]. Highly lithiated regions often undergo significant plastic deformation [67]. The electrochemically-induced stress and strain may affect the reaction rate and the Li diffusivity. The mechanical deformation thus couples with chemical reaction and Li diffusion, posing a challenging interdisciplinary problem.

The multiscale and interdisciplinary nature of electrode degradation poses significant scientific challenges in understanding the electro-chemo-mechanical process. Currently, experimental studies have been mainly focused on the battery-cell level measurement, with the post-mortem TEM/SEM characterization of lithiated-delithiated products. Even though the new *in-situ* TEM technique can offer the opportunities for researchers to real-timely track the behaviors of electrods during Li insertion-extraction cycling, information regarding the real-time nanoscale electrochemical process of the electrodes is critically missing due to the extreme challenges in constructing small-scale batteries and real-time imaging with atomic resolution. Therefore, enormous efforts have been dedicated to the development of chemo-mechanical models to understand the inherent electrochemical and mechanical coupling problems in LIBs.

At the atomistic length scale, first-principles calculations have provided the lattice constant, binding energy of Li atoms, and the migration barriers within Si and other high-capacity crystals [68-84]. In addition, the Li insertion-extraction mechanisms, structures and properties of the lithiated Li-M (M = Si, Ge, Sn) alloy phases are also studied based on density functional theory (DFT) [85-88]. However, most of these data are only valid for the dilute Li condition (where the crystalline structure remains). Atomistic simulations with the ReaxFF reactive force field that accounts for complicated bond

order, frequent bond breaking and forming during the lithiation-delithiation process are also conducted to reveal the mechanisms of the electrochemical reactions happening in high capacity electrodes and at electrode-electrolyte interface [89-93].

At the other end of length scale spectrum, continuum-level models generally couple mechanical equilibrium conditions with Li diffusion equations. Various models have been developed to describe the diffusion-induced stress in Si anode [94-98]. In all these works, the Li insertion is treated as atomic diffusion in solid electrodes, and the fundamental physics involved is the Li diffusion changes the compositions and volumes of the solid electrodes. If the volumetric change can not be accommodated appropriately, mechanical stress will be generated in the solids, and in turn affect the Li diffusion in the electrodes [99]. However, all of the aforementioned models are based on the assumption of single-phase lithiation: Li distribution varies gradually and smoothly in the electrodes, and predict only hoop compression in the outer surface layer of the solid electrodes, which is in contradiction to the experimentally observed phenomena that fracture always initiates on the outer surface of the electrodes during lithiation [20, 30, 44, 65].

Motivated by recent experimental observation that lithiation of crystalline Si nanowires (*c*-SiNWs) and nanoparticles (*c*-SiNPs) proceeds through the migration of an atomically sharp phase boundary that separates the fully lithiated amorphous shell and the intact pristine core [19, 30, 33, 55], different two-phase lithiation models have been developed to predict the large elasto-plastic deformation and stress in Si under lithiation. Zhao et al. [100] and Pharr et al. [101] simulated the Li diffusion in Si nanopillar by solving a surrogate heat conduction problem, in which the two-phase lithiation process is realized by prescribing a moving temperature field. Using the same method for the two-

phase lithiation, Ryu et al. [102] developed a cohesive zon-finite element model to simulate the anisotropic lithiation and fracture in *c*-SiNPs. However, as the movements of the reaction fronts are generated by the prescribed moving temperature field, which means the Li flow rates and directions are fixed at the beginning of the simulation, the effect of local stress on the Li reaction-diffusion (rates and directions) can not be simulated by such models. Therefore, these models are realized in a unidirectional coupling manner in which only the effect of Li reaction-diffusion on mechanical stress can be considered, whereas the effect of mechanical stress on Li reaction-diffusion is ignored. In addition, Cui et al. [103] developed a mathematical model with finite deformation kinematics and stress-diffusion bidirectional interactions considered to study the interaction between interfacial chemical reaction and bulk diffusion in binary systems by introducing an electrochemical Biot number defined by the ratio of the rate of interfacial chemical reaction and the rate of bulk diffusion. In contrast to the aforementioned models with prescribed interface movements, this model is capable of capturing the evolution of phase interface with arbitrary shapes. Moreover, Huang et al. [104] constructed a model with the interfacial chemical reaction at reaction front and Li diffusion in the lithiated shell considered in a unified manner by treating the interfacial reaction as the diffusion to investigate the stress generation in a spherical particle subjected to Li insertion. In this model, a nonlinear Li concentration-dependent function for Li diffusivity was adopted to produce a sharp phase boundary with an abrupt change of Li concentration. Nevertheless, this nonlinear diffusion model did not contain a material length scale related to the interface thickness [66] and the crystallographic orientation-dependent interfacial reaction [55] was not considered.

1.3 Scope of the Thesis

Despite the significant advance in experimental studies of high capacity anode materials, models that are versatile enough to capture the key experimental phenomena and reveal the mechanical degradation origins are still lacking. Challenge still lies in the establishing a multiscale model that concurrently incorporates the essential microstructure-deformation dynamics at all the length scales: dynamic multi-phase evolution; phase-dependent material properties; and tempo-spatial variation of large deformation, defect nucleation and growth, and failure. Therefore, models that are significant for the fundamental understanding of the deformation and fracture mechanisms in the high capacity anode materials during lithiation-delithiation process are urgently needed for the rational design of high energy density anodes in LIBs.

In the present study, a chemo-mechanical model is developed for the study of morphological evolution, stress generation, and fracture in lithiated high capacity anode materials such as Si and Ge. The model couples Li reaction-diffusion with large elastoplastic deformation in a bidirectional manner: insertion of the Li into electrode generates localized stress, which in turn mediates electrochemical insertion rates. In addition, the model incorporates several key physical features observed from TEM studies, and is thus faithful to the underlying chemo-mechanical mechanisms. The modeling framework developed herein is generic and therefore applicable to study the degradation mechanisms in a variety of high-capacity electrodes. Moreover, molecular dynamics (MD) simulations with the ReaxFF reactive force field are conducted to elucidate the failure mechanisms of lithiated single-layered graphene and single-walled carbon nanotubes (SWCNTs) with preexisting defects. The atomistic understanding of the degradation mechanisms from these simulations could subsequently lead to the rational design of electrodes with maximum reliability and lifetime extension.

The remainder of this thesis is organized as follows. In Chapter 2, a finite-strain chemo-mechanical modeling framework that incorporates several key features observed from TEM studies including the sharp amorphous-crystalline interface, anisotropic interface mobility and large deformation is developed. Using this model, lithiationinduced phase change, large deformation and fracture in SiNWs with different crystallographic orientations are simulated. In contrast to the fragile c-Si nanostructures, the tough electrochemical lithiation-delithiation behavior of individual crystalline Ge nanoparticles (c-GeNPs) studied by in-situ TEM is reported in Chapter 3. Chemomechanical modeling is conducted to investigate the mechanisms that lead to the different lithiation behaviors of c-SiNPs, c-GeNPs, and amorphous SiNPs (a-SiNPs). Chapter 4 explores the influence of the external bending on the lithiation kinetics and deformation morphologies in Ge nanowires (GeNWs). The stress dependence of both Li diffusion and interfacial reaction rate during lithiation is demonstrated by the chemo-mechanical modeling. In addition, lithiation-induced self-weakening mechanisms of graphene are investigated using MD simulations with the ReaxFF reactive force field in Chapter 5. The strong coupling between the crack-tip stress gradient and the Li migration is explored. Furthermore, the Li diffusion mediated fracture in SWCNTs with different preexisting defects is simulated in Chapter 6. The effects of the defect size, Li concentration, and loading rate on the onset fracture strain as well as the crack propagation speed are

studied. Finally, the major results and conclusions from the current study are summarized in Chapter 7, and possible extensions are also discussed.

Chapter 2

A Chemo-Mechanical Model of Lithiation in Silicon⁽ⁱ⁾

2.1 Introduction

The high-capacity Lithium (Li) ion batteries (LIBs) are critically important for portable electronics, hybrid electric vehicles, and large-scale energy storage [1, 7, 105]. This has stimulated enormous efforts to the development of new electrode materials that are not only of high energy and high power densities, but also electro-chemo-mechanically reliable [9, 11, 30, 35, 43, 44, 52, 56, 106, 107]. A number of high-capacity electrode materials have been recently studied, among which silicon stands as the leading candidate with its theoretical capacity one order of magnitude higher than conventional graphite anodes [9, 11, 27, 33, 108]. However, inherent to the high-capacity electrodes, Li insertion-extraction induces large volumetric change and stress inside the electrodes, causing degradation and cracking [14, 24, 109-111]. The issue becomes more significant when an electrode undergoes high-rate charging or discharging, which often induces non-uniform Li distribution in the electrodes. The resulting large incompatible deformation between regions with different Li concentrations tends to initiate fracture in the electrodes. Subsequent crack propagation and failure may cause the loss of electrical

⁽¹⁾ Results reported in this chapter are mainly from:

Yang, H.; Fan, F.; Liang, W.; Guo, X.; Zhu, T.; Zhang, S., J. Mech. Phys. Solids, 2014. 70(0): p. 349-361.

Yang, H.; Huang, S.; Huang, X.; Fan, F.; Liang, W.; Liu, X.H.; Chen, L.-Q.; Huang, J.Y.; Li, J.; Zhu, T.; Zhang, S., Nano Lett., 2012. 12(4): p. 1953-1958.

where, Yang, H. did all of the simulation work and data analysis.

contact between active materials, current collectors, and electrolytes, leading to fast capacity fading and poor cyclability. Chemo-mechanical degradation is one of the major challenges in the development of next-generation high-performance LIBs.

It has been recognized that nanoscale electrode materials can facilitate strain relaxation, enhance flaw tolerance, shorten Li ion and electron diffusion paths, and increase surface area for Li-electrode reaction [36, 112]. Therefore, scaling the size of electrode materials down to the nanometer range represents one of the promising strategies to drastically improve the electrode performance [27, 43, 48, 51, 113, 114]. Recent experimental studies on the size effect have demonstrated that nanoscale materials indeed exhibit better capacity retention as compared to their bulk counterparts [20, 30, 95]. The promise of nanomaterials also motivated the development of new experimental platforms for real-time studies of electrode degradation at the nanoscale. In these works, a nanoscale battery is assembled, where the electrodes are comprised of nanoparticle or nanowire arrays, or even single nanoparticles and nanowires [19, 33, 35, 44, 55-60]. The electrochemical cycling responses of the nano-battery were monitored by *in-situ* highresolution transmission electron microscope (TEM) [19, 57, 60]. This experimental setup allows real-time tracking of the tempo-spatial evolution of large deformation, crack nucleation and propagation, and phase transformation during electrochemical cycling, thereby offering a unique platform for the study of degradation mechanisms in electrodes.

Recent scanning electron microscope (SEM) and TEM studies have revealed a range of novel phenomena during lithiation of Si nanowires (SiNWs) and nanoparticles (SiNPs) [18-20, 24, 33, 55, 57, 115]. Upon lithiation, crystalline SiNWs (*c*-SiNWs) not only undergo large volume expansion (~300%), but also swell in an anisotropic manner

[18, 19, 24], with predominant expansion along the $\langle 110 \rangle$ direction, but negligibly small expansion along the $\langle 111 \rangle$ direction [19]. The anisotropic swelling results in a range of unique cross-sectional morphologies in fully lithiated SiNWs, depending on the crystallographic orientations of *c*-SiNWs [18, 19], as shown in Fig. 2-1. SEM and TEM studies further show that crack nucleates from the surface of lithiated SiNWs or SiNPs [19, 20, 30, 44]. Subsequent crack extension not only depends on the size of SiNWs and SiNPs, but also occurs along the specific directions dictated by the crystallographic structure of the pristine crystalline Si (*c*-Si) [20, 30, 44]. More recently, it has been observed that lithiation of SiNWs or SiNPs slows down as lithiation proceeds, indicating that mechanical stress generated in the lithiation process can drastically retard chemical reaction at the reaction front and/or the Li diffusion in the lithiated regions [65, 115].

Despite the rapid advance in experimental studies, models that are versatile enough to capture the key experimental phenomena and reveal their mechanistic origins are still lacking. In this chapter, a chemo-mechanical model is developed for the study of morphological evolution, stress generation, and fracture in lithiated Si. The model couples Li reaction-diffusion with large elasto-plastic deformation in a three-dimensional (3D) setting. In addition, the model incorporates several key physical features observed from TEM studies, and is thus faithful to the underlying chemo-mechanical mechanisms. The modeling framework is generic and thus applicable to study the degradation mechanisms in a variety of high-capacity electrodes.

The rest of this chapter is organized as follows. Section 2.2 discusses several key features observed in TEM experiments, which form the physical basis of the chemo-mechanical model. Section 2.3 formulates the chemo-mechanical model, with special
attention paid to the mathematical incorporation of these key physical features. Section 2.4 implements the model by finite element methods. Section 2.5 reports major numerical results on the morphological evolution and stress generation of the SiNWs under lithiation. Possible extensions of the model are discussed in Section 2.6 and conclusions are drawn in Section 2.7.



Figure 2-1. SEM [20] and TEM [19] images of anisotropic swelling and fracture in lithiated SiNWs with four different axial orientations: (a) <100>, (b) <110>, (c) <111>, and (d) <112>. Top: Cracks oriented along the axes of the SiNWs are indicated by red arrows. Bottom: The corresponding crystallographic orientations of the facets on the sidewalls of each SiNW are shown. The scale bars in the insets are 200 nm.

2.2 Key Physical Features in Lithiation of Crystalline Silicon

2.2.1 Sharp Phase Boundary

During electrochemical lithiation, Li reacts with and diffuses within Si. Since the Li mobility on the surface is much larger than that in the bulk, Li tends to first cover the surface of SiNWs or SiNPs before radial Li flow starts [19, 30, 65, 73]. Recent *in-situ*

TEM studies revealed that lithiation of *c*-SiNWs or *c*-SiNPs proceeds through the migration of an atomically sharp reaction front (~1 nm in width) that separates the lithiated amorphous shell of Li_xSi alloy and the *c*-Si core (Fig. 2-2) [19, 33, 55, 66]. The Li concentration within the unlithiated core is apparently low, evidenced by the intact lattice structure with the measured lattice spacing close to that of pristine *c*-Si [19, 33, 55]. The lithiated phase likely consists of amorphous Li₁₅Si₄ since its volume expansion is close to that of crystalline Li₁₅Si₄ [19, 55]. The lithiation reaction front is therefore identified as a phase boundary, across which an abrupt change of Li concentration occurs. Namely, the Li-poor and Li-rich phases do not transform continuously into each other with changing composition, and lithiation proceeds by the phase boundary migration. The sharp interface plays a vital role in stress generation and fracture in *c*-Si during lithiation [44, 65]. A mechanistic model thus requires a faithful description of co-evolution of the two phases with a sharp phase boundary.

2.2.2 Time Scales of Reaction and Diffusion

Lithiation of SiNWs involves two processes in series: Li diffusion through the lithiated shell and chemical reaction at the phase boundary. The characteristic time of long-range Li diffusion scales with $t_D \sim L^2/D$ [10, 112], where L and D are the sample size and the Li diffusivity in lithiated amorphous Si, respectively. On the other hand, Li-Si reaction is a short-range process involving the dissociation of the Si-Si bonds and formation of the lithiated amorphous product at the reaction front. The characteristic time scale t_R of Li-Si reaction (i.e., of reaction front migration) is L/k, where k is the rate

constant of reaction. A critical length scale, $L_{cr} = D/k$, exists. For nanometer-sized samples, $L \ll L_{cr}$. The reaction front under this condition propagates much slower than the Li diffusion behind it, and lithiation is limited by the interfacial reaction. On the contrary, for large specimens, $L \gg L_{cr}$, and lithiation is limited by diffusion. A transition between the two rate-limiting mechanisms exists at an intermediate size of L.



Figure 2-2. *In-situ* TEM experiment of lithiation of a <112>c-SiNW. (a) TEM image of a *c*-SiNW prior to lithiation. (b) Formation of a core-shell structure in a partially lithiated SiNW, where the crystalline core (*c*-Si) is surrounded by the amorphous shell (*a*-Li_xSi). A thin layer of Li₂O is formed on the outer surface of the lithiated shell. (c) The amorphous-crystalline interface (ACI), i.e., the phase boundary separating the amorphous lithiated shell and the unlithiated crystalline core, is atomically sharp (~1 nm) [55].

2.2.3 Lithiation Anisotropy

There have been debates regarding the origin of anisotropic swelling of c-Si upon lithiation when the experimental observations were first reported. Considering the coreshell structure in a partially lithiated SiNW or SiNP, the elasto-plastic properties and Li

diffusivity in the fully lithiated shell are both isotropic because of its amorphous structure. In the pristine crystalline core, the cubic structure of Si crystal renders isotropic Li diffusivity [116], but anisotropic elastic properties. Owing to the lithiation-induced strain mismatch, the crystalline core undergoes elastic deformation. The anisotropic elastic properties of c-Si could lead to stress anisotropy, which could in turn cause anisotropic reaction rate near the reaction front, considering that chemical reaction rate is generally stress-dependent. However, the order of elastic anisotropy (with elastic moduli $Y_{<111>} > Y_{<100>} > Y_{<100>}$) is inconsistent with that of lithiation-induced expansion $(\varepsilon_{<110>} > \varepsilon_{<100>} > \varepsilon_{<111>})$, which excludes the possibility of the dominant role of elastic anisotropy. In addition, the marginal anisotropy in the elastic properties (elastic moduli differ by only $\sim 10\%$ in <111> (189 GPa) and <110> (169 GPa) directions [117]) is unlikely to account for the considerable anisotropy of expansions in lithiated SiNWs (swelling in <110> is about 9 times that in <111>). This leaves only one possible origin of the anisotropic swelling: the crystallographic orientation dependence of the Li-Si reaction rate at the sharp phase boundary [100, 118].

The orientation dependence of reaction rate was recently verified by *in-situ* TEM studies [55]. It has been observed that lithiation of *c*-Si proceeds by the migration of an amorphous-crystalline interface (ACI) [19, 30, 55, 115]. The interface migration occurs through a ledge mechanism, involving lateral movement of ledges on the close-packed $\{111\}$ atomic planes [55]. These ledges are usually inclined to the ACI (except for the $\{111\}$ interface), leading to the orientation dependence of interfacial migration velocity. The *in-situ* TEM shows that the phase boundary migrates much faster along <110>

directions (several nanometers per minute) than other directions, while the interfacial migration velocity is at least one order of magnitude lower along <111> directions [55].

The orientation dependence of lithiation rate at the reaction front affects not only the morphology of the fully lithiated Si structures, but also the subsequent fracture [20, 44]. At the fastest-moving {110} interface, the large volumetric expansion occurs due to an abrupt increase of Li concentration across the interface. Such expansion tends to push the lithiated product behind the moving interface outward [44, 65, 104, 118]. As a consequence of the outward pushing normal to {110} interfaces, large incompatible strains are generated at the intersections of adjacent {110} facets (particularly near the outer surface), leading to crack nucleation at well-defined angular sites [44].

2.2.4 Lithiation-Induced Large Deformation

Lithiation of *c*-Si can characteristically results in amorphous alloys and large deformation. It is now well-accepted that lithiated Si undergoes material remodeling through plastic flow [67], generating unique deformation morphologies [18, 19, 24]. The lithiation-induced deformation is expected to be large and well beyond the applicable region of small-strain theory. Indeed, as demonstrated in the previous simulations, the small-strain theory may be still suited to approximate the morphological evolution, but inadequate to accurately predict stress distribution in the SiNWs under lithiation [118]. It is important to note that the small-strain theory predicts a nearly uniform principal stress within the lithiated shell. This would imply that crack nucleation might be equally possible at any location near the surface of the lithiated SiNWs, in contradiction with the

well-defined surface fracture sites observed in recent SEM and TEM studies [19, 20, 44]. Such inadequacy suggests that the finite-strain plasticity theory should be invoked to accurately compute stress generation during lithiation, since it is essential to use the appropriate strain and stress measures and associated constitutive relations that distinguish the reference and deformed configurations [119].

2.3 A Chemo-Mechanical Model

2.3.1 Evolving the Two-Phase Microstructure

A partially lithiated SiNWs or SiNPs with a core-shell structure can be decomposed into three numerical domains: two bulk domains, one behind the reaction front (where $c \ge c_+$) and the other in front of the reaction front (where $c < c_-$), and a diffuse interfacial domain (where $c_- < c < c_+$) with thickness δ between the two bulk domains [118], as shown in Fig. 2-3. Note that c is the Li concentration normalized by that of the fully lithiated phase of Li₁₅Si₄, with c = 1 representing Li₁₅Si₄ and c = 0 pure Si. Here, c_+ is assigned to be close to 1, while c_- close to 0. It should be stressed that Li transport in the interfacial domain occurs through chemical reactions that are characterized by the dissociation of the Si-Si bonds and formation of the amorphous Li₁₅Si₄, which are expected to differ from the atomic processes of Li diffusion in the lithiated shell [55]. Despite such a difference between reaction and diffusion, the two concurrent processes are simulated in a unified manner by treating the interfacial reaction as non-linear diffusion across a diffuse interfacial domain for numerical convenience. One should, however, bear in mind the difference in the physical processes of interfacial reaction and bulk diffusion.



Figure 2-3. Decomposition of a partially lithiated core-shell structure into three subdomains: two bulk domains, one behind the reaction front ($c \ge c_+$, red region) and the other in front of the reaction front ($c < c_-$, blue region), and the amorphous-crystalline interfacial domain ($c_- < c < c_+$) with thickness δ between the two bulk domains, where *c* is the Li concentration normalized by that of the fully lithiated phase of Li₁₅Si₄, with c = 1 representing the amorphous Li₁₅Si₄ (red region) and c = 0 pure crystalline Si (blue region).

In order to produce a sharp phase boundary with an abrupt change of Li concentration, the Li diffusivity is set to be a nonlinear function of Li concentration in the entire system:

$$D = D_0 \left[\frac{1}{\left(1 - c \right)} - 2\alpha c \right] \tag{2-1}$$

where D_0 is a diffusion constant and α is a tunable constant that controls the concentration profile near the phase boundary [19, 118]. The singular function yields

considerably large Li diffusivity in the lithiated shell (c = 1), but a finite value (D_0) close to the unlithiated core (c = 0), thereby effectively generating a sharp interface that separates the Li-poor core and the Li-rich shell [19, 55]. In order to avoid numerical singularity, D is set to be $D = 10^5 D_0$ when the value of the singular term in Eq. (2-1) exceeds 10^5 . It should be pointed out that while the strong nonlinearity of Li diffusivity is essential to produce the sharp interface, the choice of the specific functional form in Eq. (2-1) is only a matter of computational convenience [104].

In order to implement the orientation-dependent reaction rate at the reaction front during lithiation of c-Si, the reaction rate is set to depend on the local crystallographic orientation of the exposed c-Si facets within the interfacial domain ($c_{-} < c < c_{+}$). However, within the lithiated domains $(c \ge c_+)$, the diffusivity is set to be isotropic. As mentioned previously, the orientation-dependent reaction rate (or interfacial mobility) is modeled by the anisotropic interfacial diffusion across an interfacial domain between the lithiated and unlithiated regions. Based on the experimental data, the orientationdependent interfacial diffusion constants are set to be $D_{0,<110>}^F = 6D_{0,<100>}^F = 60D_{0,<111>}^F$ [118], where the associated orientations are indicated in the subscripts and the superscript "F" indicates the constant within the interfacial domain. Here the orientation-dependent interfacial diffusivities play the same role of orientation-dependent reaction rate constants when the interfacial layer is regarded approximately as a sharp interface, as discussed above. A smooth interpolation using the trigonometric functions from the above diffusion constants gives those of other directions (shown in Fig. 2-4), which are currently unavailable due to the limited experimental data.



Figure 2-4. Orientation-dependent diffusion constant (modeling the lithiation reaction rate) at the sharp amorphous-crystalline interface (ACI) on the cross sections of SiNWs with different axial orientations: <100>, <110>, <111>, and <112>.

The diffusion constant in the lithiated domain, denoted by D_0^B , is set to be the same as $D_{0,<100>}^F$, where the superscript "B" indicates the bulk domains behind the reaction front. With this setting, the diffusivity D computed by Eq. (2-1) is significantly

larger in the lithiated domain than that in the interfacial domain due to the difference in the Li concentrations of these domains. This effectively realizes the two-phase microstructure with a sharp phase boundary whose migration is rate-limiting.

2.3.2 Lithiation-Induced Elasto-Plastic Deformation

Lithiation of SiNWs or SiNPs results in a core-shell structure. The deformation in the crystalline core simply involves the elastic straining of the lattice. At the sharp reaction front, an abrupt change of Li concentration causes large chemical strains. In addition, the lithiated shell behind the reaction front further undergoes structural relaxation through elasto-plastic deformation [67], which is induced by the pushing-out effect associated with lithiation expansion at the moving, curved reaction front. Considering the lithiation-induced large deformations, the finite-strain plasticity theory is employed to characterize the deformation kinematics and the constitutive relations.

In the finite-strain plasticity framework, deformation is characterized by the elastic and plastic stretch rates (denoted by \mathbf{d}^e and \mathbf{d}^p , respectively) and spin rates (denoted by \mathbf{W}^e and \mathbf{W}^p , respectively). The total stretch rate tensor \mathbf{d} can be decomposed into three additive parts:

$$\mathbf{d} = \mathbf{d}^c + \mathbf{d}^e + \mathbf{d}^p \tag{2-2}$$

where \mathbf{d}^{c} , \mathbf{d}^{e} , and \mathbf{d}^{p} are the chemical, elastic, and plastic stretch rates, respectively [98, 120-123]. Assuming that the lithiation-induced electrochemical deformation rate is

dilational without spin and the electrochemical stretch rate \mathbf{d}^c is proportional to the increment of the Li concentration, then:

$$\mathbf{d}^c = \beta \mathbf{I} \dot{c} \tag{2-3}$$

where β is the lithiation expansion coefficient and **I** is the identity tensor. One notices that the chemical strain is analogous to the thermal strain in formulation by considering β as the coefficient of thermal expansion and *c* the temperature. Moreover, assumption is also made that the lithiated product undergoes isotropic hardening and accordingly $\mathbf{W}^{p} = \mathbf{0}$.

In the model, the unlithiated crystalline core is treated as an isotropic, elastic material, whose stress and strain rates obey the classical Hooke's law with two material constants, Young's modulus Y and Poisson's ratio v. For the lithiated phase, the isotropic elastic and perfectly plastic model is adopted to describe its constitutive response, which relates the stretch and stress rates by the following form:

$$\boldsymbol{\tau}^{\nabla e} = \frac{\hat{Y}}{1+\hat{\nu}} \left[\mathbf{d}^{e} + \frac{\hat{\nu}}{1-2\nu} \operatorname{tr}(\mathbf{d}^{e}) \mathbf{I} \right]$$
(2-4)

where "tr" denotes the trace of a tensor, τ is the Kirchhoff stress. The superscripts in $\tau^{\nabla e}$ denote the Jaumann rate of τ , for which the elastic spin is involved. Note that the Kirchhoff stress is related to the Cauchy stress σ by $\tau = J\sigma$, where J characterizes the elastic volume expansion [120]. Different from the crystalline core for which the elastic constants are fixed values, the two elastic constants, Young's modulus \hat{Y} and Poisson's ratio \hat{v} , for the lithiated product are phase-dependent, i.e., vary with Li concentration.

The plastic stretch rate, \mathbf{d}^p , obeys the associated J_2 -flow rule. Namely, plastic yielding occurs when the equivalent stress, $\tau_{eq} = \sqrt{3\mathbf{s} \cdot \mathbf{s}/2}$, reaches the yield strength, τ_Y . Here $\mathbf{s} = \boldsymbol{\tau} - \text{tr}(\boldsymbol{\tau})\mathbf{I}/3$ is the deviatoric stress tensor. In the J_2 -flow theory, the plastic stretch rate is given by:

$$\mathbf{d}^{p} = \frac{3\mathbf{s}}{2\tau_{eq}} d_{eq}^{p}$$
(2-5)

where $d_{eq}^{p} = \sqrt{2\mathbf{d}^{p} : \mathbf{d}^{p} / 3}$ is the equivalent plastic stretch rate.

The lithiated phase is modeled as an isotropic elastic and perfectly plastic material. However, perfect plasticity often leads to numerical instability in simulations. To circumvent this difficulty, the Cowper-Symonds overstress power law with appropriately chosen parameters to approximate the perfectly plastic limit is used, as:

$$d_{eq}^{p} = m \left(\frac{\tau_{eq}}{\tau_{Y}} - 1\right)^{n}$$
(2-6)

where m and n are the reference stretch rate and the rate sensitivity exponent, respectively [119].

2.3.3 Boundary Value Problem

The dynamic evolution of Li concentration, morphological change, and stress generation in lithiated Si can be simulated by solving a coupled boundary value problem. At any given time in a lithiation process, all the material points satisfy the following equilibrium equation:

33

$$\nabla \cdot \boldsymbol{\sigma} = 0 \qquad \text{in } V \tag{2-7}$$

with a traction-free boundary condition

$$\mathbf{n} \cdot \boldsymbol{\sigma} = 0 \qquad \text{on } S \tag{2-8}$$

where ∇ represents the vector differential operator with respect to spatial coordinates, **n** is the outward normal of the outer surface of the SiNW exposing to Li, *V* is the volume of the SiNW, and *S* is the outer surface of the SiNW.

As aforementioned in the previous section, the concurrent reaction and diffusion processes are simulated in a unified manner by treating the interfacial reaction as nonlinear diffusion across a diffuse interfacial domain for numerical convenience in the current model, despite the difference in interfacial reaction and bulk diffusion. Therefore, the classical diffusion equation is adopted to describe Li transport in the entire domain:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(D \nabla c \right) \qquad \text{in } V \tag{2-9}$$

The Dirichlet boundary condition is imposed on the circumference Γ of the circular cross section at one end of the SiNW:

$$c = 1 \qquad \text{on } \Gamma. \tag{2-10}$$

2.4 Numerical Implementation

2.4.1 Model Parameters

To simulate the dynamic evolution of the core-shell structure in lithiated SiNWs, the coupled chemo-mechanical model is implemented in the finite element package ABAQUS [119]. As diffusion and heat conduction are dictated by the same type of governing equation (Eq. 2-9), the Li diffusion is simulated by solving a surrogate heat conduction problem, where the normalized Li concentration c is regarded as temperature T in heat conduction [19, 100, 101, 104, 118]. Accordingly, the lithiation-induced electrochemical stretch rate \mathbf{d}^c is simulated by a thermal strain rate and the lithiation expansion coefficient β is then equivalently treated as the coefficient of thermal expansion. Using the implicit coupled temperature-displacement procedure in ABAQUS/Standard, the corresponding Li concentration and stress-strain fields are updated incrementally. Meanwhile, the user subroutine UMATHT interfaces with ABAQUS to dynamically update the diffusivities based on the instantaneous Li distribution profile.

Using the coupled chemo-mechanical model, the morphological evolutions and stress generation of the four three-dimensional SiNWs with different axial orientations (<100>, <110>, <111>, and <112> in Fig. 2-1) are simulated [18, 19]. Prior to lithiation, the cross sections of all the SiNWs are circular with a radius of *R*. Due to symmetry of the cross section, only a quarter of each SiNW is simulated with appropriately imposed symmetrical boundary conditions in order to reduce the computational cost.

All the material parameters are specified according to experimental data whenever possible. The yield stress τ_y for the fully lithiated phase, Li₁₅Si₄, is set to be 1.5 GPa [66, 67, 124]. The simulation domain is carefully meshed to ensure numerical stability and convergence. The material parameters *m* and *n* in Eq. (2-7) are set to be m = 1000 (1/s) and n = 1, respectively, which yield nearly rate-independent behavior. Young's modulus \hat{Y} and Poisson's ratio \hat{v} of the lithiated product are both assumed to linearly vary with Li concentration, i.e., from 160 to 40 GPa and from 0.24 to 0.22 [72, 77, 91, 117], respectively, as *c* varies from 0 (*c*-Si, $\hat{Y} = Y$ and $\hat{v} = v$) to 1 (the fully lithiated phase). The chemical dilational coefficient is chosen to be $\beta = 0.6$ in order to match the 300% volume expansion in the fully lithiated phase.

2.4.2 Treatment of the Interfacial Domain

The model involves a careful treatment of the interfacial domain. At any instant, the narrow interfacial domain ($c_{-} < c < c_{+}$) is identified based on the Li concentration profile. In the current model, $c_{-} = 0.02$ and $c_{+} = 0.98$ are chosen. At any point within such an interfacial domain, the local interfacial orientation is determined from the direction of the largest Li concentration gradient, i.e. that of the resultant concentration gradient vector. Based on the component of the concentration gradient vector in the cross-sectional plane, the diffusion constants D_0 along these directions can be calculated from the interpolated function of the orientation-dependent diffusion constant, as shown in Fig. 2-4. However, Li diffusivity on the surface of SiNWs, irrespective of the local interfacial orientation, is set to be two orders of magnitude larger than that in the bulk, which reflects the much faster Li diffusion on the surface of SiNWs than in the bulk. The Li concentration profile is then updated to simulate the migration of the phase boundary in the SiNWs.

As will be demonstrated later, the interfacial domain identified spans only a few elements in finite element simulations, demonstrating its sharpness. In addition, the thickness of the interfacial domain remains roughly the same throughout the simulation. One notes that the experimentally observed thickness of the amorphous-crystalline interface is about δ -1 nm [66]. The simulated interfacial domain thus conveniently defines a characteristic length scale in the finite element model that would be otherwise scale independent.

2.5 Numerical Results

2.5.1 Lithiation-Induced Anisotropic Swelling: Small Strain Model

In this section, a 3D finite element, small-strain model is used to simulate the morphological change and stress generation in SiNWs. Figure 2-5 shows the morphologies of four lithiated SiNWs with their crystallographic orientations shown in Fig. 2-1. The dynamic Li transport in the axial and radial directions of the SiNWs are indicated by the color contours, with red representing the nearly fully lithiated amorphous Si phase (Li₁₅Si₄) and blue the crystalline Si phase. For each SiNW, three subfigures respectively display the overall deformation morphology, the Li concentration profiles along the radial direction and along the axial direction. In each subfigure, a quarter of partially lithiated cross section (shaded) is displayed by an enlarged image with finite element meshes attached, showing the width of the interface is only a few elements.



Figure 2-5. 3D morphologies of the lithiated SiNWs of different axial crystallographic orientations: (a) <100>; (b) <110>; (c) <111>; and (d) <112>. The Li concentrations on the surface and different cross sections are indicated by the contours. Transition colors from red to blue indicate the reaction fronts. In each SiNW, a quarter of the partially lithiated cross section (shaded) is highlighted by an enlarged image with finite element meshes attached, showing that the width of the simulated interface is only a few elements.

As the Li diffusivity on the surface of SiNWs is much larger than that in the bulk, the surface of the SiNWs acts as a fast Li transport path. It follows that the cross sections along the axial direction are lithiated in a similar fashion: Li flows radially inward, forming a two-phase core-shell structure separated by a sharp interface. As shown in Fig. 2-5, the cross sections close to the end are fully lithiated. Within the partially lithiated cross sections, the reaction fronts form polygonal shapes. The unlithiated core tapers along the axial direction of SiNWs. The development of the faceted reaction front is due to the much higher mobility of {110} phase boundaries than others. From the fully lithiated end to the remote unlithiated end of the nanowire, the remaining core of unlithiated *c*-Si becomes progressively larger. Thus, the core-shell structures of different cross sections along the axial direction at any instant can be effectively considered as the dynamic lithiation process of a single representative cross section. It should be noted that as lithiation proceeds, only the {110} facets survive eventually at the core-shell interface. The simulated two-phase microstructure and morphological evolution of the SiNWs agree closely with the experimental observations [18, 19], as shown in Fig. 2-1.



Figure 2-6. Li flux profiles at a representative lithiation snapshot (t = 0.3) for all the four SiNWs, showing that the dominant flux in the <110> directions, a direct consequence of high reactivity of Li at the {110} phase boundary.

Figure 2-6 plots the Li flux profile on the front ends of different SiNWs at time t = 0.3, where t is normalized by the total time required to fully lithiate the front end of the SiNWs, and the flux vectors are represented by red arrowed lines (the arrow represents the direction of the flux, while the length of the arrowed lines the magnitude). The resulting flux patterns indicate that the Li diffusion in the <110> directions is considerably faster than other directions in the lithiated shell, despite of the imposed isotropic diffusivity in the lithiated shell. Such <110>-preferred flux patterns, which result from the large reaction rate at the {110} phase boundary, i.e., the high mobility of

the {110} core-shell interface, demonstrated that the current Li reaction-diffusion model can effectively capture the essential features of Li transport.



Figure 2-7. Maximum principal Cauchy stress distributions (based on small-strain theory) in the lithiated SiNWs (from left to right: <100>, <110>, <111>, and <112>) at the lithiation snapshots t = 0.3, where t is normalized time.

The maximal principal Cauchy stress (denoted by σ_1) in the four SiNWs at the lithiation snapshot t = 0.3 is shown in Fig. 2-7, where t is normalized by the total time required to fully lithiate the front end of the SiNWs. It can be found that the small-strain model captures the general trend of stress distribution in the lithiated SiNWs, i.e., the development of hoop tension in the lithiated outer shell and compression near the reaction front. However, the simulated stress distribution does not exhibit significant concentration of hoop tension in the surface layer, implying that fracture may initiate at any circumferential position at the outer surface, which contradicts with the well-defined fracture sites observed in previous experiments [19, 20, 44]. Such discrepancy arises from the small-strain theory used in the 3D simulations, to be shown in the next section.

2.5.2 Lithiation-Induced Anisotropic Swelling: Finite-Strain Model

Based on the finite-strain model, the 3D morphological change and stress evolution of the SiNWs are also simulated with the same boundary conditions as adopted in the small-strain model. Figure 2-8 plots the maximal principal Cauchy stress (denoted by σ_1) at the lithiation snapshots t = 0.3, where t is again normalized by the total time required to fully lithiate the front end of the four SiNWs. The predicted morphological changes of the cross sections for all the SiNWs due to lithiation are similar to those by the small-strain model. Importantly, the finite-strain analysis predicts concentration of hoop tension at particular angular sites of the cross sections in the SiNWs, indicating the onset fracture locations. The predicted sites of onset fracture agree with the recent experimental studies [19, 44], as shown in Fig. 2-1.



Figure 2-8. Maximum principal Cauchy stress distributions (based on finite-strain theory) in the lithiated SiNWs (from left to right: <100>, <110>, <111>, and <112>) at the lithiation snapshots t = 0.3, where t is normalized time.

As the current model involves large plastic deformation and dynamically couples Li diffusion and mechanics, the 3D model is computationally expansive, particularly when relatively fine meshes are used. Since different cross sections in each of the SiNWs are lithiated in a similar manner, a two-dimensional (2D) model may be well suited to capture the stress generation in the SiNWs. In accordance to the negligible expansion along the axial direction of the SiNWs observed in experiments [18], the plain-strain condition can be justified and imposed in the 2D simulations. The Dirichlet boundary condition c = 1 is imposed on the outer boundary of the cross section. Figure 2-9 plots the maximal principal Cauchy stress (σ_1) at four different lithiation snapshots t = 0.015, 0.05, 0.2 and 0.3, where t is normalized by the total time required to fully lithiate each of the cross sections. One notes that the stress distribution profiles on the cross sections in the SiNWs obtained by the 2D simulations agree closely to those by the 3D model, demonstrating the validity of the 2D model.



Figure 2-9. Stress contours (the maximal principal Cauchy stress) in the lithiated SiNWs. From left to right, the four columns represent the morphological changes and stress distribution in $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 112 \rangle$ SiNWs, respectively. Each column includes four simulation snapshots (t = 0.015, 0.05, 0.2 and 0.3, where t is the normalized time) of the SiNWs being lithiated.



Figure 2-10. Evolution of Li concentration and the principal stresses of two representative material points in the <100> SiNW. Both points are located at r = 0.9R in the pristine state of the SiNW, where *R* is the radius of the SiNW. Point 1 (P1) is located along the largest expansion direction (<110> direction, $\theta = 0^{\circ}$), and Point 2 (P2) along the least expansion direction (<100> direction, $\theta = 45^{\circ}$).

It should be noted that the maximal principal stress σ_1 represents the hoop component at the symmetric planes, and closely approximates the hoop component anywhere else. As seen from the stress contours, the hoop component σ_1 is tensile in the outer surfaces, while compressive near the reaction fronts. The hoop tension near the outer surface stems from the "pushing-out" effect, i.e., the large volume expansion at the reaction front causes the radial expansion and accordingly hoop stretch in the materials behind the reaction front. It is also observed that the concentrated stress develops at the early stage of lithiation. The levels of stress concentration (~1.5 τ_r) are almost the same for the four SiNWs. Interestingly, the stress concentration exclusively occurs at the angular sites between two adjacent {110} facets for all the four SiNWs. The development of such stress concentrations at the specific angular sites near the outer surface can be attributed to the pushing-out effect of the newly lithiated product from the two adjacent {110} facets at the reaction front. As the pushing-out effect generates large expansion normal to the {110} facets, the materials located at the intersection of the two adjacent {110} facets undergo large and non-uniform stretch, leading to stress concentration. The concentrated stress may well exceed the fracture strength of the amorphous lithiated Si. As a result, fracture initiates at the specified angular sites near the outer surfaces of the lithiated SiNWs.

Figure 2-10 plots the evolution of the maximal principal stress experienced by two representative material points along with that of the Li concentration at the points in the <100> SiNW of the 2D models. The two material points are located at r = 0.9Ralong the maximal ($\theta = 0^\circ$, denoted by point 1) and minimal ($\theta = 45^\circ$, a stress concentration site, denoted by point 2) radial expansion directions, respectively, of the <100> SiNW in the pristine state, as marked in the inset of Fig. 2-10. As the material points are very close to the outer surface of the SiNW, the reaction front reaches the material points in a very short time at which the Li concentration begins to rise, and rapidly reaches to unity, i.e., the fully lithiated state. Point 1 is lithiated earlier than Point 2 since the former is right along the primary Li flow direction, i.e., the <110> direction. As the reaction front sweeps through the material points, the principal stress decreases, reaches a minimum, and then rapidly increases to its maximum. For Point 1, the principal stress even changes its sign twice (from tension, compression, to tension) when the reaction front sweeps through it. As lithiation continues, the principal stresses at these two points vary insignificantly. It should be noted that Point 2 experiences a maximal stress double more than that at Point 1, clearly indicating that it is the onset site of fracture.

2.6 Discussions

The present modeling framework can be extended in several aspects, particularly regarding the stress-mediated lithiation rate and size-dependent fracture. In general, Li insertion generates hydrostatic compression both at and closely behind the reaction front in solid-state electrodes. The compressive stress may suppress Li reaction at the reaction front as well as Li diffusion behind it, thus slowing down further lithiation. Such stress-induced retardation of lithiation has been demonstrated by recent *in-situ* TEM studies: the migration of the lithiation reaction front in both SiNWs and SiNPs slowed down considerably as lithiation proceeded [65, 115]. The lithiation-induced hydrostatic compression in Si could be high enough to completely override the electrochemical driving forces on reaction and diffusion, leading to the stagnation of lithiation. Thus, the lithiation-induced stresses play an important role in the kinetics of Li insertion and extraction in electrodes, which will subsequently affect the charging and discharging rate.

Lithiation retardation can be characterized by incorporating the stress effects on the lithiation kinetics. Both the reaction rate at the reaction front and the diffusion rate in the lithiated region may be set to be stress dependent, e.g.,

$$D_{eff} = D \exp(-p\Omega / k_B T), \qquad (2-11)$$

where D is the Li diffusivity in the stress-free condition, defined in Eq. (2-1), Ω is the activation volume of Li diffusion, k_BT is the thermal energy, and p is the pressure that can be obtained from the trace of the symmetric Cauchy stress tensor σ [103, 115, 125].

Figure 2-11 shows the simulated time evolution of the lithiation depth measured at the front ends of the <110>- and <111>- oriented c-SiNWs and amorphous SiNW (a-SiNW). The lithiation depth is measured in the lithiated configuration and normalized by the thickness of the fully lithiated SiNWs. For c-SiNWs the lithiated thickness is measured in the $\{110\}$ direction, while for the *a*-SiNW in an arbitrary radial direction, as marked by the colored arrows in the deformed cross sections of the SiNWs in Fig. 2-11. The lithiation times for all the cases are normalized by that required for fully lithiating the front end of the <110>-oriented c-SiNW. For the a-SiNW, the anisotropic mobility at the reaction front is turned off in the simulation by assigning an orientation-independent constant value to D_0 in Eq. (2-1). The slopes of the curves in Fig. 2-11 indicate the lithiation rates. At the early stage of lithiation, the lithiation thicknesses of all SiNWs evolve nearly at the same high rate, corresponding to the fast surface lithiation of the nanowires. With the inward movement of the reaction front in the radial direction, lithiation-induced hydrostatic pressure p increases in order to push out the materials in the thickening shell, and consequently the effect of p becomes more significant. By reducing the reaction rate at the reaction front and the diffusivity in the lithiated shell, the compressive stress finally leads to the retardation of the lithiation process, namely, the gradually slowing down of the increasing rate of the lithiation thickness. It should be noted that the retardation effect is less intensive in the *a*-SiNW than that in the crystalline ones due to the isotropic mobility of the reaction front. The simulations clearly show that with increasing lithiation anisotropy (*a*-SiNW < <111> c-SiNW < <110> c-SiNW [118]) the retardation effect is increasingly pronounced.



Figure 2-11. Thickness evolution of the fully lithiated *a*-Li_xSi shell in the cross sections of <100>- and <111>- oriented *c*-SiNWs and an *a*-SiNW. The lithiation thickness is measured in the deformed configuration and normalized by the thickness of the fully lithiated SiNWs, while the lithiation time is normalized by that required for fully lithiating the <110>-oriented *c*-SiNW. For *c*-SiNWs the fully lithiated thickness is measured in the {110} direction, while for *a*-SiNW in an arbitrary direction due to its isotropic lithiation, as marked by the colored arrows in the deformed cross sections of the SiNWs.

It should be pointed out that stress gradient can also regulate the lithiation kinetics in solid electrodes [89, 126]. The effect of stress gradient can be incorporated into the model by relating the stress gradient to the Li flux, as shown recently [126]. These studies clearly showed the strong coupling between lithiation-generated stress and lithiation kinetics. In the following chapters, the exploitation of externally applied forces to regulate lithiation rate and rate anisotropy will be also demonstrated. Given the intimate relations between lithiation rate anisotropy and the fracture of c-Si electrodes, this study opens a possible pathway to mitigate the degradation of c-Si during electrochemical cycling.

Within the framework of finite-strain plasticity, the present model accurately predicts the locations of stress concentration, consistent with the experimentally observed crack nucleation sites in lithiated SiNWs. Once nucleated, subsequent crack propagation is size dependent, as shown in the recent experiments [30]. Such size dependence of fracture can be understood in terms of flaw tolerance in small systems. For a SiNW with a sufficiently small diameter, the energy release rate during crack extension is dominantly governed by the sample size (i.e., the diameter of cross section) rather than the flaw size, i.e., an increase of the sample size can raise the energy release rate of crack extension, given the same size of the crack. When the SiNW exceeds a critical diameter, the energy release rate becomes large enough to drive crack growth. In addition, the coupling between lithiation chemistry and crack mechanics involves the interplay between the crack-tip stress field and the local Li reaction-diffusion [89, 126]. Therefore, a detailed study of crack extension in lithiated Si that incorporates these factors is worthwhile.

2.7 Conclusions

In conclusion, a finite-strain chemo-mechanical model is formulated in this chapter to study the lithiation-induced phase change, large deformation and fracture in *c*-

Si in a 3D setting. The modeling framework incorporates several key features observed from TEM studies, including the sharp amorphous-crystalline interface, anisotropic interface mobility and large deformation. The model also couples the Li reactiondiffusion with deformation mechanics in unidirectional manner, i.e., lithiation induces strain and stress. By considering the effect of lithiation-induced stress on Li reactiondiffusion kinetics, the model can be further extended to bidirectional coupling. Though only *c*-SiNWs were simulated in this chapter, the modeling platform can be extended to *a*-Si (by turning off the anisotropic mobility of the reaction front) and other high-capacity electrode materials (with experimentally verified materials properties), as demonstrated in the following chapters.

Using the chemo-mechanical model, the morphological evolution and stress generation in SiNWs upon lithiation is simulated. The simulation results show that the anisotropic interfacial Li mobility significantly impacts the morphological changes and stress concentration in lithiated Si. Owing to the much faster reaction rate along the <110> directions, the unlithiated cores exhibit polygonal shapes with $\{110\}$ facets. The large deformation occurring at the reaction front, i.e., $\{110\}$ facets, pushes the lithiated product outward, resulting in large anisotropic swelling as well as stress concentrations at the angular sites between adjacent $\{110\}$ facets in the lithiated shell. In addition, Li insertion can induce high hydrostatic pressure at and closely behind the reaction front, as shown in the simulation results, which may explain the lithiation retardation observed by *in-situ* TEM studies. It also found that the 3D small-strain model can capture the morphological changes and the general trend of stress distribution during lithiation. In

contrast, the 3D finite-strain model captures not only the morphological evolution, but also the concentration of hoop tension, and thus predicting the onset fracture sites in the lithiated SiNWs. Since all the cross sections in the SiNWs are lithiated in a similar manner with insignificant elongation along the axial directions, a 2D finite-strain model with the plane-strain condition is demonstrated to be well suited to accurately resolve the stress concentration during the lithiation process. Such a 2D model is advantageous for its significantly reduced computational cost. Both the morphological changes and fracture sites predicted by the current finite-strain models agree well with the previous experimental studies. In addition to presenting a chemo-mechanical model for the study of lithiation-induced degradation in high-capacity electrode materials, the mechanistic understanding of microstructural evolution and stress generation in current study shed lights onto the design of next-generation failure-resistant electrodes.

Chapter 3

Tough Germanium Nanoparticles under Electrochemical Cycling[®]

3.1 Introduction

The demand for high-capacity lithium-ion batteries (LIBs) for portable electronics, hybrid electric vehicles, and large scale energy storage has stimulated the relentless search for new electrode materials with superior energy density, power density and cyclability [1, 7, 105]. Silicon (Si) is being considered as one of the leading candidates to replace current carbonaceous anodes in LIBs for its high theoretical capacity [9, 11, 27, 108]. However, Si electrodes undergo huge volume changes (~300%) induced by lithium (Li) insertion and extraction during charging-discharging process, which can lead to fracture even in the first cycle, and subsequently the rapid, irreversible capacity decay and poor cyclability [19, 20, 30]. Therefore, mechanical degradation during electrochemical cycling remains a major technical barrier for the commercialization of the Si based high-capacity electrode materials [14, 19, 20, 53, 127-130]. In addition to Si, germanium (Ge), as another group IV element, is also being treated as a promising anode material due to its unique characteristics. As shown in Fig. 1-4, the capacity of Ge is second only to that of Si [23]. More importantly, both the Li diffusivity and the electronic conductivity in Ge are much higher than those in Si [28,

⁽²⁾ Partial results reported in this chapter are from:

Liang, W.; Yang, H.; Fan, F.; Liu, Y.; Liu, X.H.; Huang, J.Y.; Zhu, T.; Zhang, S., Acs Nano, 2013. 7(4): p. 3427-3433.

where, Liang, W. conducted the in-situ TEM experiments.

131], which can enable the high-rate charging-discharging performance of Ge electrodes. Even though the high performance of Ge-based anodes has been demonstrated by recent experiments [132-135], the cyclability of Ge electrodes, which is the major concern for high-capacity LIBs, remains unclear.

In this chapter, the behavior of crystalline germanium nanoparticles (c-GeNPs) under charging-discharging cycling is studied by using *in-situ* transmission electron microscopy (TEM). The experimental results revealed that during multiple lithiationdelithiation cycles c-GeNPs of a large size range (from 100 nm to submicrometer) remained robust with highly reversible expansion and contraction, and without any visible cracking, despite ~260% volume changes. For the comparison of the lithiationdelithiation behaviors of c-GeNPs and crystalline silicon nanoparticles (c-SiNPs), the electrochemical behavior of c-SiNPs was also investigated. In stark contrast to the robust behavior of c-GeNPs, c-SiNPs exhibited the size-dependent fracture upon the first lithiation, which is consistent with the previous experimental observations [30, 65]. In addition to the *in-situ* TEM studies, a chemo-mechanical modeling is conducted to elucidate the underlying mechanisms that lead to the different behaviors of c-SiNPs, c-GeNPs, and amorphous silicon nanoparticles (a-SiNPs). Through a comparative study, the lithiation anisotropy is demonstrated to cause the non-uniform stress in the hoop direction in lithiated c-SiNPs, leading to fracture in the well-defined planes. In the absence of such lithiation anisotropy as the lithiation rate at the reaction front in Ge and a-SiNPs is nearly crystallographic orientation-independent [35, 57, 59, 61, 62, 136, 137], the c-GeNPs and a-SiNPs experience uniform hoop tension in the surface layer without the localized high stress and therefore remain robust throughout multicycling. The

findings of this study demonstrate that the Li insertion-induced high, non-uniform stresses can be mitigated through isotropic lithiation, which presents a novel mechanism of averting the fracture in high-capacity electrodes.

3.2 Experimental Methodology

In order to prepare the GeNPs used in the experiment, a Ge wafer was first ground for 30 min, and then the obtained Ge powders were dispersed in ethanol solution, followed by ultrasonic treatment. A tip-flattened Pt rod was dipped into the solution to let the GeNPs to attach onto the end of the Pt rod through surface interaction. A typical asprepared GeNP with a diameter of ~620 nm is shown in Fig. 3-1(a), which was singlecrystalline (denoted as *c*-GeNP) as demonstrated by the electron diffraction pattern (EDP) in Fig. 3-1(b). The *c*-SiNPs were prepared by following the same procedure, while the used Si powders were a commercialized product of US Research Nanomaterials, Inc.

The *in-situ* TEM study of the lithiation-delithiation cycling behavior of *c*-GeNPs and *c*-SiNPs was carried out based on an open-cell nanobattery configuration, as schematically shown in Fig. 3-1(c). The open-cell nanobattery consists of a single *c*-GeNP (or *c*-SiNP) sitting on a Pt rod as the working electrode, a small piece of bulk Li metal on a tungsten (W) probe as the counter electrode, and a native lithium oxide (Li₂O) surface layer grown on the Li metal as the solid electrolyte. During the electrochemical tests, the open-cell nanobattery was first implanted in TEM using a Nanofactory TEMscanning tunneling microscopy (STM) holder, and then a piezo-positioner was used to drive the Li₂O/Li electrode to contact the *c*-GeNPs (or *c*-SiNPs). In order to initiate and sustain the lithiation (delithiation), a bias of -2 V (+1 V) was applied to the Pt rod with respect to the W rod. Such *in-situ* TEM setup enables the real-time measurement of electrochemical reactions in electrodes during the lithiation-delithiation cycling [19, 26, 33, 35, 38, 55, 57, 59, 65, 115].

3.3 Results and Discussion

3.3.1 Experimental Results

The morphological evolution and phase transformation of an individual *c*-GeNP are shown in Figs. 3-1(d-f). At the beginning of the *in-situ* TEM experiment, a potential of -2V was applied to the *c*-GeNP with respect to the Li metal electrode in order to initiate the lithiation. Once the pristine GeNP was brought into contact with the Li₂O/Li electrode, the entire surface of the GeNP was quickly covered by Li, owing to the much higher Li diffusion rate on the surface than in the bulk of Ge, similar to the lithiation of Si [30, 57]. The GeNP then began to expand radially, as shown in Fig. 3-1(d), indicating the start of bulk lithiation. As the lithiation proceeded, Li flowed nearly uniformly from the surface to the center of the GeNP along the radial direction, forming a structure consisting of a *c*-Ge core and a lithiated shell of amorphous Li_xGe (*a*-Li_xGe) that were separated by a sharp amorphous-crystalline interface, as marked by the red dashed circle in Fig. 3-1(e). The similar core-shell structures were widely observed in the lithiation of Si nanowires (*c*-SiNWs) [19, 33] and SiNPs [30, 57]. As shown in Fig. 3-1(e), Li insertion induced a nearly isotropic volume expansion in the GeNP, leading to the change

of diameter from 620 nm (Fig. 3-1(a)) to 830 nm (Fig. 3-1(e)). The approximately uniform thickness of the obtained amorphous shell clearly indicated the isotropic lithiation in GeNPs. At 632 s, the GeNP was fully lithiated with its diameter increased to



Figure 3-1. Morphological evolution and phase transformation of an individual *c*-GeNP during lithiation. (a) Pristine *c*-GeNP with a diameter of ~620 nm. (b) The EDP indicates the GeNP is single-crystalline. (c) Schematic illustration of the *in-situ* nanobattery setup, consisting of a single GeNP as the working electrode, bulk Li metal as the counter electrode, and a naturally grown Li₂O surface layer as the solid electrolyte. (d-f) TEM snapshots showing the morphological evolution and uniform volume expansion of the GeNP upon lithiation. (d) Pristine GeNP was brought into contact with the Li₂O/Li electrode. (e) Lithiation-induced crystal-to-amorphous phase transformation, forming the structure with a crystalline core and an amorphous shell. The amorphous-crystalline interface is marked by the red dashed circle. (f) The *c*-Li₁₅Ge₄ phase formed after full lithiation to *a*-Li₁₅Ge₄, as indicated by the EDP shown in (g).

946 nm (Fig. 3-1(f)), which corresponds to ~260% volume increase, consistent with the ~280% volume increase of the fully lithiated SiNPs (a-Li₁₅Si₄) [30, 138]. However, the lithiated GeNP did not fracture even though its initial size was considerably large, which was in distinct contrast to the *c*-SiNPs that typically fracture into pieces upon lithiation

provided that the initial diameter exceeds ~150 nm [30]. As identified by the EDP in Fig. 3-1(g), the fully lithiated *a*-Li₁₅Ge₄ phase in the GeNP was finally crystallized to *c*-Li₁₅Ge₄ [139, 140]. Similar to the congruent crystallization of *a*-Li_xSi [140], the crystallization of *a*-Li_xGe to *c*-Li₁₅Ge₄ was a simultaneous process for the whole nanoparticle, and no phase boundary can be observed during the process. Such observed two-step phase transformation of *c*-Ge \rightarrow *a*-Li_xGe \rightarrow *c*-Li₁₅Ge₄ is consistent with the previous study of lithiation in *c*-GeNWs [35].

In order to investigate the cycling behavior of GeNPs, another nearly spherical shaped c-GeNP with an initial diameter of ~160 nm was selected for the in-situ TEM experiment, as shown in Fig. 3-2(a). The corresponding EDP of the GeNP confirmed its single-crystalline phase (Fig. 3-2(b)). For the lithiation of the GeNP, a bias of -1 V was first applied. After 54 s, when the *c*-GeNP was fully lithiated to *a*-Li₁₅Ge₄ (Fig. 3-2(c)), the diameter of the GeNP increased to 247 nm, which corresponds to ~260% volume increase. Then the potential was reversed to +1 V before crystallization occurred to initiate the delithiation process. The spherical a-Li_xGe NP shrunk in a uniform manner once the delithiation started, and was fully delithiated to its original size ~160 nm with the final phase identified as a-Ge (Fig. 3-2(d)). By periodically reversing the applied potential, repeated lithiation-delithiation between a-Ge and a-Li_xGe was conducted after the first cycle, as shown in Figs. 3-2(e-k) and the videos in the Supporting Information of [44]. It should be noted that the applied potential should be reversed immediately once the GeNP was fully lithiated to $a-Li_{15}Ge_4$ but before the crystallization of $a-Li_{15}Ge_4$ to ensure the further delithiate the a-Li_xGe NP. If the applied potential was held for a



Figure 3-2. Multicycling of a single *c*-GeNP. (a) Pristine GeNP with a nearly spherical shape is 160 nm in diameter. (b) EDP of the pristine GeNP indicates that the nanoparticle is single-crystalline. (c-d) First lithiation-delithiation cycle. A bias of -1 V was applied in the lithiation process. The diameter increased to 247 nm with *a*-Li_xGe formed. Then, a bias of +1 V was applied to initiate delithiation. The diameter decreased to 160 nm after full delithiation with *a*-Ge phase formed. (e-j) Second, third, and fourth lithiation-delithiation cycles showing the same behavior as the first cycle, demonstrating the cyclability of the GeNP. (k, l) Fifth lithiation and crystallization. The *a*-Li_xGe phase formed and then crystallized to *c*-Li₁₅Ge₄.
relatively long time during the lithiation stage, for instance, at the fifth cycle (Fig. 3-2(k)), the *a*-Li_xGe was crystallized to *c*-Li₁₅Ge₄ (Fig. 3-2(l)). After crystallization, the *c*-Li₁₅Ge₄ phase could no longer be delithiated even with a higher reverse potential (+2 V), manifested by the nearly constant volume before and after the reverse potential was applied. The inability of delithiation indicated a high affinity of Li with Ge in the *c*-Li₁₅Ge₄ phase.

The above experimental results indicated that the *c*-GeNPs can sustain the lithiation-delithiation induced huge volume expansion and contraction during multiple electrochemical cyclings, which demonstrated that the c-GeNPs appear to be unexpectedly tough, in distinct contrast to the fragility (*i.e.*, ease of fracture) of c-SiNPs [30, 65]. As shown in Fig. 3-3, the typical core-shell structures in a partially lithiated c-SiNP (a1-a3), c-GeNP (b1-b3), and a-SiNP (c1-c3) were compared. The original sizes of both c-Si and c-Ge NPs are around 160 nm, and a-SiNP is about 540 nm [57]. The lithiation behaviors of the NPs differ in several key aspects. First, similar to the strong anisotropic swelling observed in lithiation of c-SiNWs [19, 30, 33], the lithiation-induced swelling in c-SiNPs was highly anisotropic (Figs. 3-3(a1-a3)), which is in contrast to the nearly isotropic volume expansion of c-GeNPs (Figs. 3-3(b1-b3)) and a-SiNPs (Figs. 3-3(c1-c3)). Second, all of the NPs undergo two-phase lithiation, that is, the unlithiated pristine core and lithiated amorphous shell are separated by a sharp interface. The apparent swelling behavior of different NPs is critically governed by the lithiation reaction at the two-phase boundary [55, 62, 118]. Due to the fastest lithiation rate of the $\{110\}$ plane in c-Si [55], a hexagonal shaped unlithiated core with the survived $\{110\}$ facets appears inside the c-SiNP. The thickness of the lithiated shell is apparently

orientation-dependent, which further demonstrates the strong anisotropy of the lithiationinduced swelling. In contrast, lithiation in the *c*-GeNP and *a*-SiNP is nearly orientationindependent, as manifested by the circular shaped core and the uniform thickness of the fully lithiated shell. The nearly isotropic lithiation in *c*-Ge is consistent with the much weaker orientation-dependent wet-etching rate in *c*-Ge than in *c*-Si [136, 137].



Figure 3-3. Lithiation-induced anisotropic swelling and fracture in a *c*-SiNP versus the isotropic swelling without fracture in a *c*-GeNP and *a*-SiNP. The original sizes of both *c*-Si and *c*-Ge NPs are about 160 nm, and *a*-SiNP is about 540 nm. (a1) Partially lithiated *c*-SiNP showing the hexagon-shaped *c*-Si core with the {110} facets. (a2, a3) Fracture occurred in a late stage of lithiation. The well-defined fracture sites are indicated by red dashed circles. (b1, b2) Partially lithiated *c*-GeNP showing the rounded *c*-Ge core. (b3) Full lithiation without fracture of a *c*-GeNP. (c1, c2) Partially lithiated *a*-SiNP showing the rounded *a*-SiNP showing showing showing the rounded *a*-SiNP showing showing

According to Fig. 3-3, another striking difference among *c*-SiNPs, *c*-GeNPs, and *a*-SiNPs is their fracture behavior and cyclability. As shown in Figs. 3-3(a2-a3), the lithiated *c*-SiNP undergoes the symmetry breaking of fracture in the circumferential direction. That is, fracture occurs on the well-defined angular site (indicated by red dashed circles in Figs. 3-3(a2-a3)), which is located on one of the planes (represented by the pink dashed line in Fig. 3-4) that passes through the opposite vertices of the unlithiated hexagonal shaped *c*-Si core. Such well-defined fracture planes have also been reported in recent experiments for both *c*-SiNWs [20] and *c*-SiNPs [65], showing that the fracture sites reported here are consistent with previous experimental observations. In contrast, all the *c*-GeNPs investigated in this work and *a*-SiNPs reported in [57] are tough without any visible crack-like defects formed during electrochemical cycling. Such good electrochemical cyclability promises the GeNP as a robust, high-capacity anode material.

The previous study of *c*-SiNWs in Chapter 2 shows that intensified hoop tension σ_{θ} exclusively occurs at the angular sites between two adjacent {110} facets, as shown in Fig. 3-4, leading to the initiation of fracture at the specified angular sites near the outer surfaces of the lithiated SiNWs. Owing to the anisotropic lithiation rate in *c*-Si [55], only the fast lithiation facets (i.e., {110} facets) survive during the lithiation process. At the respective {110} facets of the reaction front, lithiation-induced volume expansion at the reaction front pushes the lithiated shell outward, leading to the large expansion normal to the facets. Materials located at the intersection of the two adjacent {110} facets undergo large and non-uniform stretch. To maintain material coherency (*i.e.*, deformation compatibility), the large intensified hoop tension σ_{θ} arises near the interface plane

(represented by the pink dashed line in Fig. 3-4) of the neighboring domains (represented by black blocks in Fig. 3-4). The concentrated hoop stress may well exceed the fracture strength of the amorphous lithiated Si, resulting surface fracture at the corresponding sites.



Figure 3-4. Development of an intensified hoop tension σ_{θ} near the fracture plane (indicated by the pink dashed line). When lithiation occurs at the respective {110} facets, lithiation-induced volume expansion at the reaction front pushed the lithiated shell outward, leading to the large expansion normal to the facets. Materials located at the intersection of the two adjacent {110} facets undergo large and non-uniform stretch. To maintain material coherency (*i.e.*, deformation compatibility), the large hoop tension σ_{θ} arises near the interface plane of the neighboring domains (black blocks).

It naturally follows that the unexpected tough behavior of the *c*-GeNPs and *a*-SiNPs [57] might be ascribed to the isotropic nature of lithiation. In order to appreciate the significance of such lithiation isotropy, it is essential to understand why the large *c*-SiNPs undergoing anisotropic swelling are fragile while the *c*-GeNPs (with a wide size range of 100 nm to submicrometer) and *a*-SiNPs undergoing isotropic swelling are not. Even though both the surface cracking and the size dependence of fracture of *c*-SiNPs

have been rationalized in the previous fracture analyses [19, 20, 30], the effects of isotropic versus anisotropic lithiation on fracture remain unclear.

3.3.2 Numerical Results

To appreciate the significance of isotropic versus anisotropic lithiation on fracture, the continuum chemo-mechanical model developed in Chapter 2 is invoked here to simulate the concurrent processes of phase transformation and stress evolution during lithiation of a c-SiNW, c-GeNW, and a-SiNW. The use of the nanowire geometry simplifies the analysis, while capturing the essential physics. Lithiation of all of the nanowires involves two concurrent processes in series: reaction at the reaction front and Li diffusion behind it. Despite the difference in the physical processes of interfacial reaction and bulk diffusion, the two concurrent processes are simulated here in a unified manner by treating the interfacial reaction as non-linear diffusion across a diffuse interfacial domain for numerical convenience. In the model, a sharp reaction front with an abrupt change of the normalized Li concentration from zero (a-Si or c-M, M = Si or Ge) to one (a-Li₁₅M₄) is generated by prescribing a concentration dependent Li diffusivity: $D = D_0 \left[\frac{1}{(1-c)} - 2\alpha c \right]$, where D_0 is the diffusion constant of Li in M, c is the Li concentration normalized by that of the fully lithiated phase of a-Li₁₅M₄, and α is a tunable constant to control the concentration profile near the reaction front. The total strain ε_{ij} consists of three parts, $\varepsilon_{ij} = \varepsilon_{ij}^c + \varepsilon_{ij}^e + \varepsilon_{ij}^p$. That is, ε_{ij}^c is the lithiation-induced electrochemical strain given by $\varepsilon_{ij}^c = \beta \delta_{ij} c$ (where c denotes the local normalized Li

concentration, β_{ij} is the expansion coefficient, and δ_{ij} the Kronecker delta with $\delta_{ij} = 1$ for i = j, and $\delta_{ij} = 0$ otherwise.), ε_{ij}^{e} is the elastic strain, and ε_{ij}^{p} is the plastic strain. In this study, β is set to be $\beta = 0.6$ for c-Si, $\beta = 0.54$ for c-Ge, and $\beta = 0.56$ for a-Si, which correspond to the ~300%, ~260%, and ~280% volume increase in the fully lithiated c-Si, c-Ge, and a-Si, respectively. The diffusion constant D_0 is set to be orientation-dependent at the sharp amorphous-crystalline interface to mimic the lithiation behavior of the <111> c-SiNW. As c-Ge and a-Si undergo nearly isotropic lithiation, the pertinent D_0 at the reaction front is set to be orientation-independent, corresponding to the isotropic lithiation rate. It should be noted that the lithiation mechanisms for a-Si and c-Si are slightly different. Lithiation of a-Si occurs by the movement of a sharp phase boundary which separates the a-Si intact phase and the amorphous Li_{2.5}Si phase (corresponding to volume expansion ~170%) in the first lithiation step. The amorphous Li_{2.5}Si is then lithiated into amorphous Li₁₅Si₄ in the second step, with a total volume expansion of ~280%. In contrast, c-Si is lithiated through the migration of a sharp reaction front that separates the lithiated amorphous shell of Li_xSi and the c-Si core. Li concentration within the unlithiated core is low, and the lithiated phase likely consists of amorphous $Li_{15}Si_4$, with ~300% volume expansion.

Figure 3-5 shows the simulated Li distribution *c* and the associated hoop stress σ_{θ} on the cross sections of different nanowires. Apparently, the different lithiation kinetics leads to differences in the volume swelling and stress generation. For anisotropic lithiation in *c*-Si, since the {110} facets undergo fastest lithiation, much stronger pushingout effect is generated along the <110> directions than any other directions, leading to large non-uniform hoop tension at the outer lithiated shell. In particular, hoop tension (σ_{θ}) at the angular sites between two adjacent {110} facets is significantly intensified (Figs. 3-5(a1-a2)) in a $\langle 111 \rangle$ c-SiNW, as large incompatible strain is developed as a result of the anisotropic pushing-out effect. These angular sites are identified as the spots of the onset of fracture, consistent with the TEM observation shown in Figs. 3-3(a2-a3). While for isotropic lithiation of c-GeNW and a-SiNW, the uniform pushing-out effect results in isotropic lithiation morphologies (Figs. 3-5(b1-b2) for c-GeNW and Figs. 3-5(c1-c2) for a-SiNW). The resulting hoop tension in the outer shell is also uniform. The lack of stress-intensified sites on the outer shell inhibits the initiation of fracture in lithiated c-GeNW and a-SiNW, which can explain why the c-GeNPs and a-SiNPs observed in the previous *in-situ* TEM studies remains tough upon cyclic lithiation and delithiation. For the simulating of the two-step lithiation in a-Si, the a-SiNW is first partially lithiated to $a-Li_{2.5}Si$, and then to $a-Li_{15}Si_4$. The first-step lithiation results in a sharp interface, while the second a diffuse interface. Figures 3-5(c1-c2) plot the Li concentration and stress distribution at the state when the two reaction fronts coincide, which represents the most critical condition but experimentally may not be realistic. The stress profile clearly shows that the two-step lithiation alleviates the abruptness of the interface and hence the incompatible stress at the interface. The pushing-out effect is also weaker, and hence reduced hoop tension in the outer shell, as compared to the lithiation generated stress in the c-GeNW (Figs. 3-5(b1-b2)). This explains the tough behavior of micron-sized *a*-Si during lithiation in previous studies [57, 61].



Figure 3-5. Chemo-mechanical modeling of the core-shell structure and stress generation in the cross section of a lithiated nanowire, showing the effect of the lithiation anisotropy. (a1) Orientation-dependent interfacial reaction rate in <111>c-SiNW leads to a hexagonal shaped reaction front in the cross section of the nanowire, represented by the transition colors from red to blue. (b1, c1) Isotropic interfacial reaction rate results in circular shaped reaction fronts in the cross sections of *c*-GeNW and *a*-SiNW. Li concentration in (a1) and (c1) is normalized by that of Li₁₅Si₄, while the one in (b1) is normalized by that of Li₁₅Ge₄. (a2, b2, c2) Hoop stress (σ_{θ}) profiles in cross sections of <111>c-Si (a2), *c*-Ge (b2), and *a*-Si (c2) nanowires. Lithiation anisotropy causes the intensified hoop tension at the angular sites between two {110} adjacent facets in the <111>c-SiNW (a2), while such intensified tension is absent in the other two nanowires (b2 and c2).

3.4 Conclusions

The electrochemical cycling behavior of individual *c*-GeNPs and *c*-SiNPs was studied with *in-situ* TEM in this chapter. The experimental results indicated that the *c*-GeNPs involves a two-step phase transformation upon lithiation: c-Ge $\rightarrow a$ -Li_xGe $\rightarrow c$ -Li₁₅Ge₄, with a ~260% volume increase, which is consistent with previous electrochemical tests. Tough behavior of the *c*-GeNPs was demonstrated by the fast lithiation-delithiation multicycling of the GeNPs with huge volume expansion and contraction. In particular, the current experiments showed that the *c*-GeNPs, as *a*-SiNPs, remained robust without fracture in multiple cycles with a wide size range (from 100 nm to submicrometers), which is in distinct contrast to the size-dependent fracture of *c*-SiNPs upon the first lithiation.

Based on the chemo-mechanical model, comparative study of the lithiation behavior of the *c*-SiNPs, *c*-GeNPs and *a*-SiNPs was conducted to appreciate the significance of lithiation kinetics on the deformation and fracture of different NPs. Due to the orientation-dependent lithiation rate, *c*-SiNPs undergo highly anisotropic lithiation. Such lithiation anisotropy is demonstrated to cause the intensified non-uniform hoop stress in outer lithiated shell of SiNPs, leading to fracture at the angular sites between two adjacent {110} facets. In the absence of such lithiation anisotropy, the *c*-GeNPs and *a*-SiNPs experience isotropic lithiation, and subsequently uniform hoop tension in the surface layer without the localized high stress. As the lack of stress-intensified sites on the outer shell can inhibit the initiation of fracture, the *c*-GeNPs and *a*-SiNPs remain robust upon cyclic lithiation and delithiation. In addition, the two-step lithiation in *a*- SiNPs can further alleviate the abruptness of the interface and hence the incompatible stress at the interface, which can lead to the tough behavior of *a*-SiNPs with the size even up to micronmeter.

As demonstrated in the current study, lithiation anisotropy is the leading factor account for the fragile behavior of c-Si during electrochemical cycling. Therefore, eliminating the lithiation anisotropy by amorphization presents a novel pathway to mitigate the mechanical degradation in high-capacity electrode materials. While previous study showed that lithiation of the {110} facet in c-Si involves the step-by-step ledge flow on the inclined, close-packed {111} layers [55], the lithiation-induced atomic arrangements in c-Ge and a-Si remain unclear. Thus, the atomistic origin of the different lithiation kinetics (isotropy or anisotropy) warrants further study in the future.

Chapter 4

Bending-Induced Symmetry Breaking of Lithiation in Germanium Nanowires $^{\ensuremath{\mathbb{S}}}$

4.1 Introduction

Insertion of secondary species into solid electrodes constitutes the primary energy-storage mechanism for modern battery systems [1, 7, 141, 142]. Understanding the insertion-induced chemo-mechanical degradation of the host materials has become a central focus of the present battery research [14, 19, 20, 30, 38, 44, 105, 143]. Much like other physiochemical processes such as oxidation and corrosion in metals, electrochemical cycling of electrodes features intimate coupling between insertion kinetics and mechanical stress: insertion of the secondary species generates localized stress, which in turn mediates electrochemical insertion rates [65, 89, 90, 115, 126]. This coupled effect is particularly strong in high-capacity electrodes in which a large amount of secondary species are inserted and extracted during electrochemical cycling. As a well studied example, crystalline silicon (c-Si), a negative electrode material with a theoretical capacity 10-fold higher than graphite [11, 17, 23], undergoes ~300% volume expansion and generates large localized tensile stress on its surface during electrochemical lithiation [19], leading to size-dependent surface fracture [30, 65]. Reciprocally, lithiation-induced

[®] Results reported in this chapter are mainly from:

Gu, M.; Yang, H.; Perea, D.E.; Zhang, J.-G.; Zhang, S.; Wang, C.-M., Nano Lett., 2014. 14(8): p. 4622-4627.

where, Gu, M. conducted the *in-situ* TEM experiments; Yang, H. did all of the data analysis and simulation work.

mechanical stress causes retardation or even arrest of lithiation [65, 115]. Understanding the coupled effect is therefore imperative for capacity retention and cycle life extension of the high-rate lithium-ion batteries (LIBs).

While the coupled effect in the electrochemical cycling of electrodes has long been recognized, the strong effect of the electrochemical reaction rate on the degradation of electrode materials has only been recently appreciated through the distinctly different lithiation behaviors of crystalline germanium (c-Ge) and c-Si [44]. Ge, another Lialloying negative electrode material with a high capacity (1384 mAhg⁻¹) second only to Si [23], undergoes ~260% volume increase (i.e., the volume of the fully lithiated product is ~360% of the original structure) upon fully lithiation [44]. Both the electron conductivity and Li diffusivity in Ge are much higher than those in Si [28, 131], rendering Ge an attractive high-rate electrode material [132-135, 144-146]. Recent in-situ transmission electron microscopy (TEM) studies revealed that lithiation of both c-Si and c-Ge proceeds by the motion of an atomically sharp two-phase interface: the lithiated amorphous phase progressively consumes the crystalline phase, forming a core-shell structure [19, 44, 55, 62]. Differently, the electrochemical lithiation rate in c-Si is crystallographic orientation dependent [18, 19, 24], as opposed to the isotropic lithiation in c-Ge [35, 44, 62], despite the similar crystalline structures of these two crystals. Consequently, c-Si undergoes anisotropic swelling, leading to crack nucleation and growth at well-defined angular sites of the outer surface of the Si crystals [19, 20, 44, 65], in distinct contrast to the isotropic swelling and tough behavior of c-Ge throughout the entire lithiation process [35, 44, 62]. The same correlation between isotropic lithiation and high toughness was recently observed in amorphous Si [57, 61], further

demonstrating the critical role of the lithiation rate anisotropy on the degradation of the electrodes. The rate-dependent chemo-mechanical behavior suggests that controlling the electrochemical reaction rate represents a new pathway for the design of durable high-capacity LIBs.



Figure 4-1. Morphological evolution of a free-standing GeNW under lithiation. (a) Schematics of the *in-situ* nanobattery setup, consisting of a single GeNW as the working electrode, bulk Li as the counter electrode, and a native Li₂O surface layer on the Li metal as the solid electrolyte. (b) A pristine *c*-GeNW with a diameter of 50 nm. (c-e) TEM snapshots showing the uniform lithiation in the radial direction, forming core-shell structures. (f) Li distribution map obtained by EELS mapping at the region marked by the red rectangle in (d); the dark region corresponds to the crystalline core of the cross section.

4.2 Experimental Methodology

Using *in-situ* TEM studies, the control of the lithiation rate in GeNWs by the external bending is demonstrated in this chapter. The GeNWs used in this study were

grown using chemical vapor deposition (CVD), which has been widely used to fabricate SiNWs. The GeNWs were doped with phosphorous for enhanced electrical conductivity. The diameter of the GeNWs ranges from 50 to 220 nm, and the length from 2 to 10 μ m. The *in-situ* TEM was carried out based on an open-cell nanobattery configuration, which consists of a single GeNW as the working electrode, bulk Li as the counter electrode, and a native lithium oxide (Li₂O) surface layer grown on the Li metal as the solid electrolyte, as schematically shown in Fig. 4-1(a). The nanobattery device was implanted in TEM using a Nanofactory scanning tunneling microscopy (STM) holder. An overpotential ranging from -0.5 V to -2 V was applied to drive the Li ions across the Li₂O solid electrolyte for lithiation. The *in-situ* TEM study enables real-time imaging of electrochemical reactions in GeNWs.

4.3 Results and Discussion

4.3.1 Experimental Results

Figures 4-1(b-e) show the TEM images of a free-standing *c*-GeNW with an initial diameter of 50 nm at different lithiation stages. As soon as the Li metal touched the GeNW (Fig. 4-1(b)), Li quickly diffused over a long distance along the GeNW surface within several seconds before bulk lithiation in the radial direction occurred (see Fig. 4-1(c) and Movie S1 in Supporting Information of [147]), owing to the much higher Li diffusion rate on the surface than in the bulk of Ge, similar to the lithiation of Si [19, 44, 57, 58, 65, 115]. The GeNW then started to expand (Fig. 4-1(d)) radially, indicative of

bulk lithiation, forming a structure consisting of a *c*-Ge core and a lithiated shell of amorphous Li_xGe (a-Li_xGe) [62]. Similar core-shell structures have been widely observed in lithiated SiNWs and Si nanoparticles (SiNPs) [19, 30, 55, 57, 65]. Previous studies revealed that lithiation of c-Ge proceeds by a two-step phase transformation: (c-Ge \rightarrow a- $Li_xGe \rightarrow c-Li_{15}Ge_4$ [35, 44]. The volume increase of the free-standing c-GeNW due to lithiation was measured to be $\sim 260\%$, which is consistent with previous studies [44], indicating that the lithiated product was likely to be $c-\text{Li}_{15}\text{Ge}_4$. These structural observations are also corroborated by the spatial distribution of Li probed by the electron energy loss spectroscopy (EELS) (Fig. 4-1(f)). It can be noted that lithiation proceeded in an axisymmetric manner in the radial directions at any axial positions, in contrast to the orientation dependent lithiation in c-Si [18, 19, 24]. As a result, the unlithiated core should be of the circular shape for all the cross sections. Throughout the lithiation process, the GeNW remained straight, indicative of minimal axial stress imposed to the nanowire during the lithiation process. It is observed that the thickness of the lithiated shell at a given lithiation time was nearly the same at different axial positions, further demonstrating much higher surface diffusivity of Li than the bulk diffusivity. Thus, the cross sections of c-GeNW at any different axial locations were lithiated in a similar manner.

Previous TEM studies demonstrated that self-generated stress during lithiation causes lithiation retardation in c-Si [115, 148]. On the basis of the coupled effect of the mechanical stress and the electrochemical lithiation rate, externally applied load might also mediate the electrochemical lithiation rate in the same manner as lithiation self-generated stress in the GeNWs. To see this, the GeNWs were brought into contact with

the Li metal for lithiation. As soon as lithiation started, the GeNWs were pushed against the Li metal electrode using a piezoelectric nanomanipulator, as shown in Fig. 4-2. The pushing force effectively bent the GeNWs while the GeNWs were being lithiated, generating a complex stress state in the GeNWs with the mixed components of bending and axial compression. The stress profile is thus radially non-uniform in the bent region such that one side of the GeNW undergoes compression and the other undergoes tension. Owing to the axial compression, the neutral plane is not the central plane of the GeNW, but shifted to the tensile side. Panel A of Fig. 4-2 (and Movies S2 in Supporting Information of [147]) displays an initially tapered GeNW (Fig. 4-2(a1)) pushed to the left (i.e., the tensile side is on the left) during lithiation. The diameter of the uniform portion of the GeNW is ~220 nm. The dark contours shown in Figs. 4-2(a1-a2) correspond to the strain induced diffraction contrast. Lithiation of the bent GeNW also generated a coreshell structure (Figs 4-2(a2-a4)), similar to the free-standing GeNW, where the red dashed lines mark the boundaries between the a-Li_xGe shell and the c-Ge core. However, the reaction front propagated asymmetrically on the tensile and compressive sides, with a noticeably higher lithiation rate on the tensile side than the compressive side. As a result, the radially uniform core-shell structure observed in the free-standing GeNW was broken in the bent GeNW. As lithiation continued, the constraint to the volume expansion along the axial direction generated increasingly higher compressive stress, which, together with the lithiation self-generated compressive stress at the reaction front, resisted further lithiation. When the combined compressive stress reached a critical value, lithiation of the GeNW was completely arrested, leaving an unlithiated core in the GeNW. This asymmetric lithiation resulted in a non-uniform core-shell structure, featuring a thicker



Figure 4-2. TEM snapshots showing the symmetry-breaking in lithiation of three representative GeNWs. The GeNWs were pushed against the Li metal to create bending during the lithiation processes, leading to lithiation asymmetry. The unlithiated crystalline cores in the GeNWs are outlined by the dashed red lines. Panels A and B: the GeNWs were pushed to the left. Panel C: the GeNW was pushed to the right.

lithiated shell (~213 nm) on the tensile side and thinner on the compressive side (~65 nm) at the bent region, as shown in Fig. 4-2(a4). It should be noted that bending-induced nonuniform contact conditions between the GeNW and the Li source biased the Li diffusion distance from the Li source to the tensile and compressive sides. However, This small biased distance should not be responsible for the symmetry-breaking of lithiation observed in the experiments since surface diffusion of Li is much faster, making the time scale associated with the biased distance negligibly small.

The bending experiments with other GeNWs were repeated, and similar results were observed, as shown in panels B and C of Fig. 4-2 and the associated Movies (Movies S3 and S4) in Supporting Information of [147]. In panel B, the GeNW with a diameter of ~220 nm was pushed to the left, and its lithiation morphology was similar to the GeNW in panel A. As lithiation came to a complete stop, the lithiated thicknesses on the tensile and compressive sides were 200 nm and 98 nm, respectively. In panel C, the GeNW with a diameter of ~200 nm was pushed to the right, and correspondingly, lithiation proceeded at a much higher rate along the right side than the left side of the nanowire, as shown in Figs. 4-2(c2) and (c4). At the end of lithiation, a small unreacted core remained on the left side of the nanowire. At the snapshot of 84 s, the lithiated thickness on the right side is 90 nm, compared to the 194 nm thickness on the right side.

To further appreciate the stress effects on the lithiation kinetics, the timedependent thickness of the lithiated shells in the GeNWs is investigated. It should be noted that the lithiation kinetics may depend on the diameter of the GeNWs, the doping conditions, the extent of pushing, and the applied overpotential, all of which may vary for different GeNWs, rendering direct comparisons of the lithiation kinetics infeasible for different GeNWs. Hence, the analysis below will be focused on the general trend of the stress effects on the lithiation kinetics.

Figure 4-3 plots the time-dependent normalized thickness of the lithiation shell for the bent and free-standing GeNWs, where the slopes of the curves indicate the lithiation rates. The thickness is normalized by the diameter of the corresponding pristine GeNW. For the free-standing GeNW (II in Fig. 4-3(a)), the lithiation thickness is measured at a representative cross section of the *c*-GeNW shown in Fig. 4-1. The lithiation started rather fast (~1.13 nm/s), but gradually slowed down (~0.06 nm/s) as lithiation proceeded, exhibiting lithiation retardation. Similar lithiation retardation behavior has been previously observed in c-SiNPs and c-SiNWs [65, 115], and has been understood as a result of suppressed lithiation rate and Li diffusion due to the lithiation self-generated compressive stress at the reaction front and in the lithiated shell, respectively. For each bent GeNW (I in Fig. 4-3(a), III and IV in Fig. 4-3(b)), two distinct cross sections at different axial positions are chosen, one located at the highly curved point, and the other at the straight portion (bending free) of the GeNW, as marked, for instance, in Figs. 4-2(b3) and (b4), respectively. Owing to the symmetry breaking at the curved segment, the lithiated thicknesses of the tensile and compressive sides are plotted separately, as shown in Fig. 4-3. From all the three curves associated with the bent GeNW, lithiation started with a relatively high speed (>2.5 nm/s), and slowed down gradually to a rather low speed (<0.1 nm/s). The initial lithiation rate for the tensile side of the cross section of the bent point is the highest, manifested by the steepest slope of the curves. The data points for the straight point fell between those for the tensile and compressive sides, indicating an intermediate stress state of this cross section. It can be

noted that the curve for the straight point is closer to that for the compressive side of the curved cross section, indicating that the GeNW globally underwent axial compression. Furthermore, after a fast lithiation regime, the lithiation kinetics curves for all the three cross sections become flat, indicating strong lithiation retardations. By comparison, lithiation retardation in the bent GeNW is apparently stronger than that of the free-standing GeNW since the pushing force also generated considerable axial compression in the bent GeNW.



Figure 4-3. Lithiation kinetics of the GeNWs. (a) Time-dependent normalized lithiation thickness of the bent GeNWs (I: the GeNW shown in panel B in Fig. 4-2) and the free-standing GeNW (II: the GeNW shown in Fig. 4-1). (b) Normalized lithiation thickness of two bent GeNWs (III: the GeNW shown in panel C in Fig. 4-2, and IV: the GeNW shown in Movie S5 in Supporting Information of [147]). The thickness is normalized by the diameter of the corresponding pristine GeNW.

4.3.2 Numerical Results

For a quantitative understanding of the bending induced symmetry breaking in the lithiation rate in GeNWs, the chemo-mechanical model developed in Chapter 2 is

extended to simulate the lithiation process in the GeNWs. In the model, a sharp reaction front (interfacial domain) with an abrupt change of Li concentration from zero (c-Ge) to one $(c-Li_{15}Ge_4)$ is generated by adopting a concentration dependent Li diffusivity: $D = D_0 \left[\frac{1}{(1-c)} - 2\alpha c \right]$, where D_0 is the diffusion constant of Li in Ge and α is a tunable constant to control the concentration profile near the reaction front. The model identifies three computational sub-domains: the lithiated shell and unlithiation crystalline core, separated by the sharp two-phase interfacial domain. Since GeNWs undergo nearly isotropic lithiation, D_0 is set to be orientation-independent within the interfacial domain. Moreover, Li diffusivity on the surface of GeNWs is set to be two orders of magnitude larger than that in the bulk, which reflects the much faster surface diffusion than that in the bulk of GeNWs. To incorporate the stress effects in the lithiation kinetics, both the reaction rate at the reaction front and the diffusivity in the lithiated region is set to be stress-dependent, i.e., $D_{eff} = De^{-p\Omega/k_BT}$, where D_{eff} is the effective diffusivity, Ω is the activation volume of Li diffusion, $k_{\rm B}T$ is the thermal energy, and p is the hydrostatic pressure that can be obtained from the trace of the Cauchy stress tensor.

The interfacial domain separates the unlithiated, elastic *c*-Ge core and the lithiated *c*-Li₁₅Ge₄ shell that undergoes large-plastic deformation. The total strain ε_{ij} in the chemo-mechanical model consists of three parts, $\varepsilon_{ij} = \varepsilon_{ij}^e + \varepsilon_{ij}^p + \varepsilon_{ij}^c$. That is, ε_{ij}^e is the elastic strain, ε_{ij}^p is the plastic strain, and ε_{ij}^c is the lithiation-induced electrochemical strain given by $\varepsilon_{ij}^c = \beta \delta_{ij} c$, where *c* denotes the local normalized Li concentration with c = 1 representing the Li₁₅Ge₄ phase while c = 0 the pure Ge phase, β is the expansion coefficient, and δ_{ij} is the Kronecker delta ($\delta_{ij} = 1$ for i = j, and $\delta_{ij} = 0$ otherwise.). In order to generate ~260% volume increase in Ge due to lithiation, β is set to be $\beta = 0.54$. To simulate the dynamic evolution of the core-shell structure in the lithiated GeNWs, the Li diffusion equation is coupled with the mechanical equilibrium equations within the framework of elasto-plasticity. The Young's modulus and yield stress are set to be Li concentration dependent, varying from 130 to 30 GPa and from 1.0 to 0.2 GPa, respectively [85, 149, 150].



Figure 4-4. Simulation setup of a GeNW under lithiation. (a) Solid model used in the simulation, consisting of a rigid substrate representing the counter electrode and a single GeNW. The bottom tip of the GeNW is fully covered by Li, and external pushing force is applied on the top end of the GeNW to bend the GeNW before lithition. (b) Finite element mesh adopted to discretize the solid model.

As shown in Fig. 4-4(a), a rigid substrate that represents the counter electrode is placed at the tapered end of a GeNW to mimic the boundary conditions in the

experiments. External force is applied to the top end of the GeNW to bend the GeNW before lithiation. Meanwhile, the surface-to-surface contact interaction (with lateral friction) is applied between the top surface of the substrate and the outer surface of GeNW. In order to simplify the model and ignore the Li diffusion across the contact surface, the Li source is set at the bottom tip of the GeNW (c=1). In addition, the symmetry boundary condition (about the x-y plane) is used to reduce the computational cost of the model. Therefore, only half of the solid model is considered in the simulation, and discretized by 8-node brick element, as shown in Fig. 4-4(b). The coupled chemomechanical model is implemented in the finite element package ABAQUS [119]. Using the implicit coupled temperature-displacement procedure in ABAQUS/Standard, the corresponding Li concentration and stress-strain fields are updated incrementally. Meanwhile, the user subroutines are used to interface with ABAQUS to dynamically update the diffusivities based on the instantaneous Li and stress distribution profiles.

A series of sequential snapshots of the simulated GeNWs during lithiation under external loading are displayed in Fig. 4-5. Figures 4-5(a1-a5) show the Li concentration profiles at different lithiation stages, while Figs. 4-5(b1-b5) the corresponding hydrostatic stress profiles, $\sigma_h = tr(\sigma)/3$, where $tr(\sigma)$ is the trace of the Cauchy stress tensor σ . To better show the bending induced symmetry breaking in lithiation, the Li concentration profile and the stress distribution of the cross section at the point of the largest curvature are also plotted at different lithiation stages. The numerically predicted morphological evolution of the GeNW during the lithiation processes under the externally applied loadis available in the Supporting Information (Movie S6) of [147]. Starting from the pristine *c*-



Figure 4-5. 3D chemo-mechanical modeling of the lithiation kinetics and stress generation in a GeNW subject to bending. (a1-a5) The Li concentration profiles at different lithiation stages; (b1-b5) The corresponding hydrostatic stress concentration profiles. The symmetry breaking in lithiation is clearly shown by both the longitudinal and cross-sectional views of the Li concentration and stress profiles. (c) Lithiation kinetics of the simulated GeNW. The lithiation thickness is normalized by the diameter of the simulated GeNW, and the time is normalized by the total time for the cross section to be fully lithiated.

GeNW (Figs. 4-5(a1) and (b1)), axially applied external force bends the GeNW (Figs. 4-5(a2) and (b2)), resulting in tension on the left side and compression on the right side at the bent region. The top-left corner is also compressed as a result of the pushing. Figures 4-5(a2-a5) show the dynamic Li transport in the axial and radial directions of the GeNW, with the red color representing the nearly fully lithiated phase (c-Li₁₅Ge₄) and blue the c-Ge phase. As the Li diffusivity on the surface of the GeNW is much higher than that in the bulk, the surface of the GeNW acts as a fast Li transport path. It follows that the Li always covers the surface of the GeNW first, then flows radially inward, forming a coreshell structure separated by a sharp interface, marked by the transition color between red and blue.

Figures 4-5(b2-b5) plot the corresponding stress profiles at different lithiation stages. It should be noted that the resulting stress profile in the GeNW is a superimposition of the lithiation-generated stress and that caused by the external pushing force. Similar to the lithiated free-standing SiNWs, the unlithiated core undergo tension, while the two-phase interface undergoes compression (See Figs. 4-5(b3-b5)) [118, 151], indicating that the lithiation-generated stress dominates the stress profiles of the core-interphase in the GeNW; whereas the applied bending mostly influences the stress profile of the outer and inner surface layers at the highly curved regions. As the hydrostatic compression retards both reaction and diffusion while hydrostatic tension enhances them, the symmetry of lithiated pattern observed in bending-free GeNW is broken by bending, as shown in both the longitudinal and the cross-sectional views. Consequently, the lithiation proceeds appreciably faster on the left side (tension side) than on the right side (compression side) of the GeNW in both radial and axial directions. Therefore, an

asymmetrical core-shell is generated, as shown by the Li concentration profile of the cross section at the bent region in Fig. 4-5. At the end of the lithiation (Figs. 4-5(a5) and (b5)), the cross section become elliptically shaped with an unlithiated core being located closer to the compressive side, further demonstrating the symmetry breaking in the lithiation process. The lithiation kinetics in the simulated GeNW is shown in Fig. 4-5(c). Compared with Fig. 4-3, these curves show the same trends: lithiation started with a very high speed and slowed down gradually, illustrating the consistence between the theoretical and experimental results.

4.4 Conclusions

In summary, the influence of the external bending on the lithiation kinetics and deformation morphologies in GeNWs is investigated in this chapter. It was found that free-standing GeNWs undergo isotropic lithiation. Lithiation self-generated internal stress due to the incompatible strain at the reaction front causes lithiation retardation in the free-standing GeNWs, similar to SiNWs and SiNPs. Bending a GeNW during lithiation breaks the lithiation symmetry, enhancing the lithiation rate on the tensile side while suppressing it on the compressive side, both in the radial and the axial directions. Chemo-mechanical modeling corroborates the experimental observations and suggests the stress dependence of both Li diffusion and interfacial reaction rate during lithiation.

The external load mediated lithiation kinetics opens new pathways to improve the performance of electrode materials by tailoring lithiation rate via strain engineering. As anisotropic lithiation constitutes the primary origin for the fracture of c-Si, external

forces, such as bending, might be applied to suppress the lithiation anisotropy, therefore mitigating fracture. The current findings also suggest that pre-tension may counteract with the self-generated compressive stress in the electrodes during lithiation, thereby improving the rate performance of the LIBs. Moreover, as an electrode is of essentially multi-components, local mechanical incompatibility among different components, particularly due to the large volume expansion of the high-capacity active materials, generates highly localized compressive stress that may subsequently result in poor rate performance and capacity loss of the battery. Therefore, active materials should be appropriately spaced such that certain extent of free expansion is permitted to avoid buildup of high compressive stresses.

Moreover, the bending-induced symmetry-breaking of lithiation may be exploited to the design of novel battery system by active, reversible bending. The battery system can be as simple as a three-layer thin film, two pre-lithiated Ge layers separated by a solid electrolyte layer. Upon bending, the chemical potential of Li on the convex side (tensile side) is higher than the concave side, leading to the Li flux to the convex side. Bending the thin film to the opposite direction reverses the flux direction. For Ge, the voltage of such bending activated battery can be deduced from the lithiation rate difference between the tensile and compressive sides of the thin film, as shown Fig. 4-3. Lithiation rate $\gamma = \gamma_0 e^{-\Delta E/k_B T}$, where γ_0 is a rate constant, $k_B T$ is the thermal energy, and ΔE is the activation energy barrier for Li-Ge reaction at the reaction front. The activation energy barrier is referenced from the energy state of the *a*-Li₁₅Ge₄, and is a function of the local stress state. A tensile stress lowers the barrier, while a compressive stress raises it. Assuming that the reference energy states are the same for the tensile and compressive sides of a bent GeNW (i.e., *a*-Li₁₅Ge₄), one notes that the chemical potential difference $\Delta \eta = k_B T \ln(\gamma_T/\gamma_C)$, where γ_T and γ_C are the lithiation rates on the tensile and compressive sides of the bent thin film, respectively. For a bending sensitive material, lithiation for the compressive side may be completely arrested, giving rise to a very large γ_T/γ_C and $\Delta \eta$, corresponding to a workable voltage of the bend-to-power battery. Going beyond Li based system and considering the system with other pre-inserted secondary species (hydrogen, sodium, etc.), bending of the thin film may also modify the chemical potentials of these secondary species, leading to the flux of the inserted species from the compressive side to the tensile side. Therefore, the mechanically controlled flux of the secondary species will feature a novel energy harvesting mechanism through mechanical stress.

Chapter 5

Self-Weakening in Lithiated Graphene Electrodes⁴

5.1 Introduction

Graphene and carbon nanotubes (CNTs) not only possess outstanding mechanical properties and electronic characteristics, but also hold significant promise as anode materials in lithium (Li) ion batteries (LIBs) [152-158]. Due to their high electrical conductivity, they have been used as conducting additives to other active materials in electrodes [22, 159]. Because of their unique geometries, CNTs and layered graphene possess enhanced energy storage capacities as compared to the conventional Li-graphite anodes [160-163]. Owing to their great flexibility and high fracture strength, they are also expected to exhibit longer cycle life than conventional carbonaceous anodes [164, 165].

Recent experimental studies evidenced that CNTs undergo mechanical degradation upon electrochemical cycling, and showed that CNTs were broken into smaller pieces after up to a few hundred or thousand cycles [38, 166, 167]. More recently, Liu et al. reported that lithiation drastically embrittles multi-walled carbon nanotubes (MWCNTs) [38], but not layered graphene [56, 130]. It was argued that the different mechanical responses stem from the geometrical constraints of MWCNT and layered graphene. For MWCNTs, the inter-wall Li intercalation causes ~6% hoop strain

⁽⁴⁾ Results reported in this chapter are mainly from:

Yang, H.; Huang, X.; Liang, W.; van Duin, A.C.T.; Raju, M.; Zhang, S., Chem. Phys. Lett., 2013. 563(0): p. 58-62.

where, Yang, H. did all of the simulation work and data analysis.

[38]. In contrast, graphene in layered geometry can freely bend into the third dimension [56], thereby suppressing the buildup of high in-plane stretching energy that would cause fracture. Despite the obvious difference in the lithiated multi-layered graphene and MWCNTs, the embrittlement of MWCNTs remains to be understood from a mechanics perspective, given the fact that a pristine CNT can sustain an in-plane strain up to 20% or even larger [168].

During lithiation of an MWCNT, Li intercalation into the graphene layers generates tensile stress in the hoop direction. The intercalated Li can be regarded as adatoms of the graphene layers, which also chemically weakens the graphene. Previous molecular orbital theory calculations showed that the presence of a single Li weakens the pristine graphene by ~30% [38]. Owing to these weakening factors, small cracks may nucleate, either homogeneously, or from preexisting atomic vacancies. The nucleation processes are beyond the scope of the present study. Instead, molecular dynamics (MD) simulations is carried out herein to elucidate the lithiation-induced failure mechanisms of monolayer graphene, with a focus on the effect of Li on the propagation of a preexisting crack in monolayer graphene. While the focus of the present study is lithiated monolayer graphene, the modeling results can be straightforwardly extended to CNTs by taking into account of the curvature effects. It is shown that the stress gradient at the crack tip drives Li adatoms migrating toward the crack tip. The aggregation of Li at the crack tip lead to two consequences: weakening the crack-tip bond due to the local chemical Li-C reaction and causes stress relaxation of the high Li-concentration region. Through MD simulations, it is identified that the chemical weakening effect is the dominant factor on the crack propagation in graphene. Moreover, the stress-diffusion coupling effect and the

crack-tip Li-aggregation induced fracture behavior are universal in the degradation of electrodes. The current studies offer a fundamental guidance to the cycle life extension of CNT- and graphene-based anodes in LIBs, and shed light on the failure mechanisms of other important anode materials such as Si.

5.2 Methodology

In the current MD simulations, the interatomic interactions are modeled by the ReaxFF reactive force field. The ReaxFF combines a bond-distance/bond order relationship with a geometry-dependent charge calculation, and provides a highly transferable method, applicable to covalent, metallic and ionic materials and their interfaces [169-171]. It generally fits not only thermodynamic properties at equilibrium states, but also kinetic properties including reaction barriers, both from first-principles based simulations. It has been adequately shown that the ReaxFF can provide an accurate account of the chemo-mechanical behavior of the hydrocarbon systems, while capable of treating thousands of atoms [91, 92, 172, 173]. The accuracy of the ReaxFF is tested after introducing Li into the hydrocarbon system. For instance, the migration barrier from one hollow site (the center of the hexagons) to another on a monolayer graphene calculated by the ReaxFF differs only 3% from the density functional theory (DFT) calculations [174, 175]. The functional form of the ReaxFF and parameters are given in Supplementary of [89].

To simulate Li-mediated crack propagation in graphene, a size-reduced model (1910 carbon atoms in total) consisting of a small circular-shaped domain cut around a

crack tip is adopted [176, 177], as shown in Fig. 5-1. In classical fracture mechanics, the asymptotic stress profile σ_{ij} for a plane-stress condition in the region sufficiently close to a crack tip can be written as:

$$\sigma_{ij} = \frac{K_1^{\text{app}}}{\sqrt{2\pi r}} \Theta_{ij}(\theta)$$
(5-1)

where *r* and θ are the polar coordinates with the origin *O* sitting at the crack tip, Θ is the known angular dependent function, *i* and *j* are the two Cartesian coordinate indices. Note that the asymptotic stress at the crack tip is dominated by a single loading parameter, i.e., the applied stress intensity factor (SIF) K_1^{app} , independent of the geometry of the specimen. Such a domain at the crack tip is known as the *K*-dominant zone. In the simulation model, the domain size is chosen such that its outer boundary falls in the *K*dominant zone. Such a small system can effectively model a long crack that extends selfsimilarly under applied *K* load with considerably reduced computational cost.

To generate the asymptotic stress profile described in Eq. (5-1) in the atomic system around a crake tip, the crack-tip displacement consistent with the asymptotic stress field is imposed on the atoms. To begin with, the pristine graphene system is dynamically relaxed at 10 K free of any constraints using the Berendsen thermostat. Starting from the relaxed system, atoms about 3 Å from the outer boundary (red dots in Fig. 5-1) are held fixed, while the remainder of atoms is set free. All the atoms in the system are then displaced according to the displacement field of the crack-tip asymptotic solution dictated by the applied SIF, with the origin *O* taking as the center of the circular graphene:



Figure 5-1. The size-reduced simulation model for analyzing the lithiation induced fracture in graphene. The circular domain can be loaded by prescribing the displacement field in Eq. (5-2), where the red dots represent the carbon atoms that are fixed, while the green dots are free carbon atoms. In determining the mobility of Li adatom, a dummy atom at the crack tip (purple) is connected to the Li adatom (gold) at the far field with a virtual spring of high stiffness.

$$\begin{cases} u_x \\ u_y \end{cases} = \frac{K_1^{\text{app}}}{2\mu} \sqrt{\frac{r}{2\pi}} \left(\kappa - \cos\theta\right) \begin{cases} \cos(\theta/2) \\ \sin(\theta/2) \end{cases}$$
(5-2)

where μ is the shear modulus of the lattice, $\kappa = (3-\nu)/(1+\nu)$, and $\nu = 0.4$ is the Poisson's ratio directly obtained from MD simulations. Due to the applied $r^{1/2}$ -dependent displacement, a crack appears with the crack tip at *O*. The stress distribution of the strained circular graphene can be obtained by evaluating the Virial stress at all the atomic sites, followed by the interpolation over the entire graphene surface [178]. The

simulations demonstrate that the Virial stress distribution agrees very well with the continuum asymptotic stress field (only hydrostatic stress is plotted as an example) that desired to mimic, as shown in Fig. 5-2(a), demonstrating the validity of the model.



Figure 5-2. Stress-mediated stability of Li adatom. (a) The pressure profile at the crack tip obtained from continuum fracture mechanics $(P \propto \cos(\theta/2))$; (b) Virial stress profile at the crack tip; (c) the stability map. From green to red colors the stability of the Li adatom increases. The high-stability domain at the crack tip is inconsistent with the high-pressure contour in (a) and (b), suggesting that shear stress and possibly the free crack edges play additional roles in the stability of the Li adatom.

5.3 Results and Discussion

5.3.1 Li Stability on a Cracked Graphene

Upon successfully setting the stress field at the crack tip, the stability and mobility of an adatom Li under the stressed environment of the crack tip is next determined. An adatom Li is placed at different hollow sites and then the binding energy is computed by imposing the *K*-dominant displacement field at prescribed *K* values. In order to calculate the energy, the system is dynamically relaxed at low temperature (10 K) with and without the Li adatom. For a graphene consisting of *n* carbon atoms, the binding of a Li adatom can be expressed by:

$$Li + C_n \to LiC_6 + C_{n-6} \tag{5-3}$$

where C_n denotes the pure graphene, the product on the right side of the arrow is the graphene with a Li adatom. The energy difference $\Delta E = E(LiC_6 + C_{n-6}) - E(Li) - E(C_n)$ gives rise to the binding (formation) energy of the Li adatom. Interpolation of the binding energy over the entire simulation model gives rise to a stability map, as shown in Fig. 5-2(c). The map clearly shows that the closer the Li adatom to the crack tip, the higher the thermodynamic stability of the system. It should be noticed that the Li stability map is not fully consistent with the high-pressure concentration profile at the crack tip. The inconsistency suggests that the shear stress and the free edges (crack surface) may play a certain role in the Li stability.

5.3.2 Migration Pathways and Kinetic Barriers of Li on a Cracked Graphene

The migration barriers of Li adatoms from the far field to the crack tip are further investigated in order to evaluate the Li mobility under the stress gradient at the crack tip. A fixed dummy point is chosen at the bridge site of the crack-tip bond because of its higher stability than the crack-tip hollow site. A virtual harmonic spring is then generated to link the dummy point and Li adatom at the far field on the graphene (as shown in Fig. 5-1). The equilibrium length of the spring at the beginning is set to be the initial distance between the dummy point and the Li adatom. The equilibrium length of the spring is then decreased incrementally, followed by system energy minimization at each step until the Li adatom moves to the dummy point. The stiffness of the spring is set to be very high such that at each step the bond length is highly constrained to the equilibrium length of the spring, while the bond can freely rotate in the 3D space, thereby enabling the exploration of the minimum energy path. Due to the high stiffness, the energy stored in the spring at each step is negligibly small. The energy landscape along the minimum energy path can be then determined from the total system energy and the spring length (i.e., reaction coordinate). Figure 5-3 shows the migration paths and barrier of the Li adatom along two directions: $\theta = 0^{\circ}$ and 45° .

Similar to the Li stability, the mobility of the Li adatom increases as it gets closer to the crack tip, manifested by the increasingly reduced migration barrier. Figure 5-3(a) depicts the migration paths of the adatom Li initially placed at three representative positions on the graphene ($\theta = 0^\circ$, 45°, and 60°). For the Li adatom placed along the direction of $\theta = 0^\circ$ and 60° (not shown), the adatom Li migrates along a straight path,
i.e., the [1 100] direction. However, for the Li adatom placed at the direction of $\theta = 45^{\circ}$, the adatom Li adopts a non-straight migration path: rather than migration along $\theta = 45^{\circ}$ direction to reach the crack-tip hollow site, the Li adatom take two $\theta = 60^{\circ}$ migration path segments, connected by a horizontal migration path. Figure 5-3(b) plots the corresponding migration energy landscapes for the adatom Li placed. In general, the migration barrier decreases as the adatom moves toward the crack tip. The calculations further show that the migration barrier also decreases with the increase of the applied stress intensity factors, as shown in Fig. 5-4.



Figure 5-3. The mobility of the Li adatom. (a): The migration paths (minimum energy paths) for a Li adatom initially placed along $\theta = 0^{\circ}$ (path indicated by a sequence of pink dots) and $\theta = 45^{\circ}$ (path indicated by a sequence of blue dots) migrating toward the crack-tip hollow site; (b) The migration energy landscapes corresponding to the two migration paths.



Figure 5-4. Load dependent migration barrier of the Li adatom ($\theta = 0^{\circ}$). As the applied load (stress intensity factor $\hat{K}_{I} = K_{I}/2\mu$) increases, the migration barrier decreases.

The above analysis shows that Li diffusion to the crack tip is both thermodynamically and kinetically favored, driven by the stress gradient around the crack tip. The stress-driven Li diffusion therefore causes the concentration of Li around the crack tip, i.e., the Li concentration gradient is in the opposite direction of the stress gradient: $\nabla c \propto \nabla P$, where $P = -(\sigma_{rr} + \sigma_{\theta\theta})/3$ is the pressure. The Li distribution has two possible consequences on the fracture of the graphene: (a) the Li adatom at the crack tip may significantly weaken the crack-tip bond, giving rise to a reduced bond strength, and therefore a reduced fracture strength; and (b) concentrating Li at the crack tip may cause local stress relaxation [126]. Both the consequences modulate the onset condition of the crack propagation.

5.3.3 Chemical Weakening and Crack-Tip Stress Relaxation

It is conceived that the Li adatoms at and around the crack tip may reduce the crack-tip C-C bond strength and at the same time disturb the stress distribution. In order to explore the coupled effects and assess how aggregation of Li at the crack tip modifies the fracture behavior of the graphene, four configurations are considered with different Li concentrations around the crack tip, forming a crystal core embedded in an outer pristine graphene shell, as shown in Fig. 5-5. Configuration Ω_0 is simply the pristine circular graphene sheet without any Li adatoms (not shown); configuration Ω_1 is the graphene sheet with a single adatom placing at the hollow site of the crack tip (Fig. 5-5(a)); configuration Ω_2 is the graphene sheet with LiC₆ around the crack tip and all the Li are placed on one side of the graphene (Fig. 5-5(b)); and configuration Ω_3 with LiC₃ around the crack tip (Fig. 5-5(c)) [81, 83]. The difference in the fracture strength between Ω_1 and Ω_0 gives rise to the chemical weakening effect of the single adatom at the crack-tip; while the difference between $\Omega 1$ and Ω_2 , and Ω_3 to the effect of Li aggregation on the fracture strength. It should be noted that it has raised heated debates as to the maximal concentration of Li on a graphene surface [179, 180]. Instead of intending to fuel the debates, the current study is focused on the chemo-mechanical consequence of concentrated Li at the crack tip.

Fracture loads at which the first C-C bond at the crack tip breaks for the four configurations are calculated by numerically determining the critical stress intensity factor \hat{K}_1 . Systematic simulations in this study show that the fracture loads are 0.86 for configuration Ω_0 , 0.75 for configuration Ω_1 , 0.71 for Ω_2 , and 0.70 for Ω_3 . The fracture



Figure 5-5. Chemical weakening and stress relaxation due to Li aggregation to the crack tip, demonstrated by the profiles of Virial stress for different Li concentrations at the crack tip. Top row from left to right: Configuration Ω_1 to Ω_3 . Li adatoms are around the crack tip. For Ω_3 , the Li adatoms on the different sides of graphene are marked by different colors. Bottom row from left to right: hydrostatic stress of the configurations corresponding to the top row.

load for Ω_1 is significantly lower than that for Ω_0 , indicating that the strong chemical weakening effect of the Li adatom to the crack-tip C-C bond. With increasing Li concentration at the crack tip, the fracture load decreases, further confirming the weakening effects of the Li adatoms on the graphene surface.

In addition to the chemical weakening effect, concentrating Li adatoms on the crack tip also perturbs the stress around the crack tip. To verify this effect, the hydrostatic stress on the carbon atoms around the crack tip is calculated using the Virial formula for the three cases (Ω_1 , Ω_2 , and Ω_3), as shown in Figs. 5-5(a2-c2). Indeed, the hydrostatic stress is moderately relaxed due to the aggregation of Li adatoms around the crack tip. The stress level suggests the magnitude of the driving force for the crack propagation. Thus, stress relaxation due to the presence of Li adatoms should theoretically lead to an increase of the fracture load, opposite to the chemical weakening effect. The calculated fracture loads, however, decrease with increasing Li concentration. This suggests that the chemical weakening effect overshadows the stress relaxation effect. It should be noted that with increasing Li concentration, the reduction in the fracture load decreases. For example, the fracture loads for Ω_2 and Ω_3 are nearly the same. This indicates that the stress relaxation becomes increasing more pronounced with further increased Li concentration. It can be followed that the stress relaxation would become the dominant factor and the fracture loads would increases beyond a critical Li concentration.

5.4 Conclusions

In conclusion, lithiation-induced fracture mechanisms of graphene are

investigated using MD simulations with the ReaxFF reactive force field in this chapter. The new ReaxFF can be used for atomistic study of phase transformation, Li diffusion, defect nucleation and growth etc., of a wide range of carbonaceous materials. Simulation results show that the stress gradient around the crack tip drives the Li migration toward the crack tip, leading to the aggregation of Li around the crack tip. The aggregation of Li locally reduces the bond strength on the one hand, and causes stress relaxation at the crack tip on the other. The former reduces the fracture strength, while the latter reduces the fracture driving force (and hence increases the fracture strength). In the case of lithiated graphene, the former factor is dominant. Taking together of the stress-gradient driven Li migration and subsequent reduced fracture strength, lithiated graphene exhibits a self-weakening mechanism that causes the fracture of the graphene.

It is worth to point out that the strong coupling between the crack-tip stress gradient and the Li migration, as well as the subsequent weakening/strengthening effects are universal for all the electrodes upon lithiation. Giving Si as an example, the stress gradient will lead to the concentration Li at the crack-tip. However, due to the large volume expansion (~300%) upon lithiation, the stress relaxation effect may be dominant over the chemical weakening effect [126]. As a result, concentration of Li may arrest propagating crack. The current studies shed lights on the lithiation-induced embrittlement of MWCNTs and pave the way to mitigate the degradation of graphene-based anode materials in LIBs.

Chapter 6

Lithiation-Induced Corrosive Fracture in Defective Carbon Nanotubes⁵

6.1 Introduction

Carbon nanotube (CNT) is being considered as one of the high-power and highenergy electrode materials in advanced lithium (Li) ion batteries (LIBs) due to its superior electrical conductivity and high surface area as compared to the bulk graphite [152, 153, 157, 158, 160, 181]. Because of their excellent mechanical flexibility and extremely high fracture strength, CNTs have also been expected to possess longer cycle life than the conventional carbonaceous anode materials [164, 182, 183]. However, recent *in-situ* transmission electron microscopy (TEM) studies evidenced that lithiation drastically embrittles multi-walled CNTs (MWCNTs), manifested by the sharp fracture edges as well as apparently low fracture strain [38], opposite to the highly reversible deformability of pristine CNTs [184, 185]. The drastic embrittlement motivated an important question as to whether defects would pre-exist in the MWCNTs of the experiments or nucleated during the experimentation, and what roles these defects might play in the embrittlement of the lithiated CNTs.

Defects are known to influence the performance of CNT-based electrodes in several aspects. For a pristine MWCNT, diffusion of Li from its open ends to its center

⁽⁵⁾ Results reported in this chapter are mainly from:

Huang, X.; Yang, H.; Liang, W.; Raju, M.; Terrones, M.; Crespi, V.H.; van Duin, A.C.T.; Zhang, S., Appl. Phys. Lett., 2013. 103(15): p. 153901-4.

where, Yang, H. did all of the simulation work and data analysis.

constitutes the only channel for Li intercalation into the interfacial spacings of the MWCNT [80, 186-188]. Due to the long diffusion distance, a long, pristine MWCNT thus may have less competitive charging-discharging rates. However, the presence of defects may enhance the charging-discharging rates of MWCNTs since Li may be able to diffuse through the defects, a shortcut to the center of the MWCNTs [166, 189-193]. In addition, the presence of a defect generates a local stress field around it, which may create a chemical potential gradient that drives Li diffusion toward the defect [89, 177]. The aggregated Li subsequently weakens the C-C bonds around the defect, acting as a corrosive agent that modulates crack nucleation and propagation [89, 126]. Therefore, a defect in a CNT thus carries a dual role upon lithiation: mechanically weakening the CNT while modulating Li diffusion and distribution. Moreover, the dual characters may be strongly coupled: the stress gradient around a defect directs Li diffusion and subsequently weakens the defects. Such a complicated interplay between defects and Li diffusion has remained elusive and merits a detailed study.

In this chapter, molecular dynamics (MD) simulations with ReaxFF reactive force field [89, 169, 172] are conducted to uncover the lithiation-mediated corrosive failure mechanisms in defective single-walled CNTs (SWCNTs). The ReaxFF combines a bonddistance/bond-order relationship with a geometry-dependent charge calculation, and provides a highly transferable method, applicable to covalent, metallic and ionic materials and their interfaces [169, 170]. As the ReaxFF generally fits not only thermodynamic properties, but also kinetic properties including reaction and diffusion barriers, both from first-principles based simulations, it has been adequately shown to provide an accurate account of the chemo-mechanical behavior of the Li/C systems, while computationally much more efficient than first-principles simulations [89, 170].

6.2 Methodology

To study the effect of defect size on the embrittlement of lithiated CNTs, two representative types of defects in a (18, 0) zigzag SWCNT are chosen: a single vacancy and a hole-like defect created by removing 10 carbon atoms [80, 187, 194-197]. Mechanical degradation by both types of defects has been widely studied in previous research [168, 198-200]. In the current MD simulations, periodic boundary condition is applied in the axial direction of the SWCNT. The length of the CNT is 7.2 nm (~1200 carbon atoms in total). Li atoms are randomly added to the outer surface of the SWCNT with varying concentrations, as shown in Fig. 6-1. Prior to loading, the system is dynamically equilibrated to its lowest energy state. Thereafter, the SWCNT is uniaxially stretched at a constant stretching rate of 0.01 Å/ps until the SWCNT breaks into two pieces. Throughout the simulations the system temperature is maintained at 300 K using the Nosé-Hoover thermostat.

6.3 Results and Discussion

Figure 6-1 depicts the fracture process of the SWNCTs with the two types of defects at four different Li concentrations: Li:C = 0, 1:36, 1:12, and 1:6. Zero Li concentration corresponds to a pure carbon structure. An interesting observation is that Li

atoms actively participate in the fracture of the CNTs. For the hole-like defect (Panel A, b, c, and d), Li tends to aggregate around the hole before fracture initiates. Some Li atoms even reach the inner surface of the CNT via through-role diffusion [80, 194]. The number of Li atoms aggregated around the hole depends on the Li concentration (until it reaches a saturation limit), leading to the different levels of weakening [89]. As a result, the onset fracture strain decreases with increasing Li concentration. For instance, at a 10% tensile strain, the Li-free SWCNT remains intact, while the SWCNT with high Li density (Li:C = 1:6) already breaks into two pieces, and for the SWCNTs with relatively low Li densities (Li:C = 1:36 and 1:12), fracture is initiated but not completed. Once the crack is initiated, the stress field in the CNT is dynamically modified as crack propagates. Driven by the potential difference associated with the dynamically modified stress profile, Li tends to diffuse toward the newly cracked surfaces and the crack tip by depleting those on the pristine part of the CNT. This active role of Li atoms on the fracture process will be further evidenced in the stress-strain relations and the time-evolving Li distribution in the CNT, as discussed in the next. For the single-vacancy defected SWCNT (Panel B), the small size of the single vacancy limits the number of Li atoms it can accommodate. It also inhibits through-defect diffusion toward the inner surface of the CNT [80, 194]. Thus, the weakening effect is relatively low as compared to the hole-like defect, and appears to be insensitive to the Li concentration, and leading to the roughly the same onset fracture strain for all the Li concentration. In addition, the fracture occurs rather abruptly and crack propagates rapidly until the CNTs completely break. For all the simulations presented above, no dislocations are observed during the fracture process, indicating that the fracture is purely brittle.



Figure 6-1. Fracture of defective (18, 0) SWCNTs with varying lithium (Li) concentrations. The green dots represent carbon atoms, while the purple dots represent Li. The applied tensile strains are indicated. (A) The SWCNT with a hole-like defect formed by removing 10 carbon atoms. Prior to crack propagation, Li aggregates to the hole. During crack propagation, Li flows to the newly cracked surface and crack tip, dynamically weakening the crack and modulating the crack propagation. The SWCNT with different Li concentrations breaks at different fracture strains. (B) SWCNT with a single vacancy defect. Fracture occurs abruptly for all the cases, and Li diffusion plays an insignificant role once the crack is initiated. Except for the Li-free case, for all the other cases with different Li concentrations the SWCNT breaks at approximately the same fracture strain.



Figure 6-2. (a) Stress-strain curve of the SWCNTs containing a hole-like defect with different Li densities under tensile loading. (b) Three fractural states of SWCNTs showing a "wait-and-go" fracture behavior of SWCNTs with a low Li density (Li:C = 1:12).

Figure 6-2(a) shows the stress-strain curves of the SWCNT with the hole-like defect. For the Li-free SWCNT and that with a high Li concentration (Li:C = 1:6), fracture occurs rather abruptly, manifested by a sudden drop of the stress to zero at a fracture strain of 14.08% and 7.15% (as listed in Table 6-1), respectively. While the brittle fracture behavior for the Li-free SWCNT is anticipated, the fast crack propagation of the SWCNT with the high Li concentration indicates that the saturated Li weakens the propagating crack at anywhere the crack-tip extends without requiring Li diffusion and redistribution. In contrast, crack propagation in the SWCNTs with relatively low Li densities (Li:C = 1:36 and 1:12) involves active Li participation, exhibiting a "wait-and-go" fracture behavior and an increased stretchability, as shown in Fig. 6-2(b). At an applied strain beyond the onset of fracture, the system arrives at state (1) at which the

crack is arrested. Further stretching of the CNT results in insufficient stress buildup at the crack tip to break the crack-tip C-C bond. The crack is thus at a waiting state for Li atoms to arrive by diffusion to weaken the crack tip bond. At state (2), new Li atoms finally arrive at the crack tip, chemically weaken the crack-tip C-C bond, the crack propagation resumes. At state (3), the bond at the crack tip breaks, and the crack is again at the waiting state since there are no Li atoms at the new crack tip. Such a "wait-and-go" process repeats until the CNT breaks into two pieces. The "wait-and-go" fracture process results in increased stretchability and fracture toughness (indicated by the area underneath the stress-strain curve).

		Onset fracture	Rapture	Fracture
Defects	Li:C	strain (%)	strain (%)	strength (%)
Hole	0	14.08	14.29	107.90
Hole	1:36	7.82	10.80	49.07
Hole	1:12	7.03	15.11	44.27
Hole	1:6	7.15	7.73	43.94
SV	0	15.49	15.71	124.77
SV	1:36	12.53	12.75	88.78
SV	1:12	12.52	12.87	80.10
SV	1:6	13.55	13.78	75.13

Table 6-1. The onset fracture strain, rapture strain, and fracture strength of defective (18, 0) SWCNTs with varying Li concentrations (SV: single vacancy).

The stress-strain curves of the single-vacancy defected SWCNTs with different Li densities are shown in Fig. 6-3. It can be found that for the single-vacancy defected SWCNTs the stress suddenly drops to zero at the fracture load for all the cases without

exhibiting the "wait-and-go" fracture phenomenon. Owing to the smaller weakening effect of the single-vacancy defect than that of the hole-like defect, the fracture stress is quite high. Upon reaching the fracture stress, the large elastic energy accumulated in the SWCNTs is released abruptly, causing fast crack propagation. The fast crack propagation leaves insufficient time for Li diffusion and redistribution. As a result, active participation of the Li atoms in the fracture process is not as obvious as in the hole-like defected SWCNTs, and the fracture behavior for all the SWCNTs are similar, independent of Li concentration. It should be noted that the fracture strain for the case of Li:C = 1:6 is ~1% higher than the other two cases with relatively low Li concentrations. The slightly increased fracture strain may possibly be due to the enhanced stretchability of the pristine part of the CNT at high Li concentration.



Figure 6-3. Stress-strain curves of the SWCNTs containing a vacancy defect with different Li densities under tensile loading.



Figure 6-4. Active lithium (Li) diffusion on the surface of SWCNTs with a hole-like (a) and single-vacancy defect (b). For both (a) and (b), Li:C = 1:12.

To further illustrate the active role of Li diffusion in the fracture of the SWCNTs, the dynamic distribution of Li on the surface of the SWCNTs during the loading process is plotted in Fig. 6-4, with the Li concentration equals to Li:C = 1:12. The hole-like defect (a) accommodates more Li atoms than the single-vacancy defect (b) prior to loading (red lines). Considerable Li atoms diffuse through the hole and arrive at the inner surface of the CNT (green line). Such through-defect Li diffusion is inactive for the single-vacancy defected CNT. Upon uniaxial stretch, Li atoms diffuse to the inner surface of the CNT, possibly due to the enlarged hole size and reduced crossing barrier for Li. As crack propagates, the spatial distribution of Li atoms changes rapidly, with significant Li atoms diffusing from the outer and inner surfaces to the newly created fractured surfaces driven by the chemical potential gradient. While for the single-vacancy defected SWCNTs, Li distribution remains nearly unchanged until complete rapture occurs.

As MD simulations clearly demonstrate that the active role of Li atoms in modulating fracture of CNTs depends on the relative time scales of the Li diffusivity and the crack propagation speed, it follows that the fracture behavior of the lithiated CNTs is also loading-rate dependent. Figure 6-5 depicts the stress-strain curves of the hole-like defected SWCNT under two different stretching rates: 0.05 Å/ps and 0.1 Å/ps, and with three different Li concentrations: Li:C = 0, 1:12, and 1:6. For the Li-free case and that of high Li concentration (Li:C = 1:6), the loading rate effect is insignificant. The loading rate independence for the high Li concentration case is due to the fact that saturated Li atoms can weaken the crack at anywhere the crack tip extends without requiring longrange Li diffusion, same as the inactive role of Li diffusion in crack propagation of the CNT with high Li concentration. In contrast, the rate dependence is more pronounced at an intermediate Li concentration (Li:C = 1:12) because Li redistribution dynamically modulates the weakening extent of the initial hole and the propagating crack. As a result, a higher loading rate yields higher fracture strength because the Li atoms do not have sufficient time to diffuse toward the hole to weaken it. Moreover, a higher loading rate (0.05 Å/ps) results in a sudden drop of the fracture stress for the similar reason. In contrast, a lower loading rate (0.01 Å/ps) results in a lower fracture stress and the "waitand-go" fracture behavior because diffusion time scale is comparable with the loading rate.



Figure 6-5. Loading rate effect on the lithiation-induced weakening of SWCNTs.

6.4 Conclusions

In conclusion, systematic MD simulations are performed in this chapter to explore Li diffusion mediated fracture in SWCNTs containing two types of defects, singlevacancy and hole-like defect. Simulation results show that Li diffusion actively modulates the onset of fracture and crack propagation. The active role of Li diffusion depends on the defect size and Li concentration on the CNT. In essence, the defect size and Li concentration set the onset fracture strain as well as the crack propagation speed. The relative time scales of crack propagation speed and Li diffusion dictate whether Li may actively participate in crack propagation. For the same reason, the failure mechanism of the defected CNTs is loading rate dependent. Interestingly, simulations demonstrate that CNTs at an intermediate Li concentration with a large defect, such as an atomic hole, fracture with a relatively slow crack propagation speed, which allows dynamic weakening the extending crack tip through Li diffusion and redistribution. The active Li participation causes a "wait-and-go" fracture behavior, leading to significantly increased stretchability. The failure analysis of the defective CNTs upon lithiation provides fundamental guidance to the lifetime extension of CNT-based anode materials.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

A finite-strain chemo-mechanical model is formulated to study the lithiationinduced phase transformation, morphological evolution, stress generation and fracture in high capacity anode materials such as Si and Ge. The model couples Li reaction-diffusion with large elasto-plastic deformation in a bidirectional manner: insertion of the Li into electrode generates localized stress, which in turn mediates electrochemical insertion rates. Several key features observed from recent TEM studies are incorporated into the modeling framework, including the sharp interface between the lithiated amorphous shell and unlithiated crystalline core, crystallographic orientation dependent electrochemical reaction rate, and large-strain plasticity.

Using the chemo-mechanical model, the morphological evolution and stress generation in different crystalline SiNWs upon lithiation is simulated. By faithfully predicting the anisotropic swelling of lithiated SiNWs observed from previous experimental studies, the simulation results demonstrate that the anisotropic interfacial Li mobility significantly impacts the morphological changes and stress concentration in lithiated Si. Owing to the much faster reaction rate along the <110> directions, the unlithiated cores exhibit polygonal shapes with {110} facets. The large deformation occurring at the reaction front, i.e., {110} facets, pushes the lithiated product outward, resulting in large anisotropic swelling as well as stress concentrations at the angular sites between adjacent {110} facets in the lithiated shell. In addition, Li insertion can induce high hydrostatic pressure at and closely behind the reaction front, as shown in the simulation results, which can explain the lithiation retardation observed by *in-situ* TEM studies. The simulation results show that the larger the lithiation anisotropy, the more conspicuous the retardation effect will be. It also found that the 3D small-strain model can capture the morphological changes and the general trend of stress distribution during lithiation. In contrast, the 3D finite-strain model captures not only the morphological evolution, but also the concentration of hoop tension, and thus predicting the onset fracture sites in the lithiated SiNWs. Since all the cross sections in the SiNWs are lithiated in a similar manner with insignificant elongation along the axial directions, a 2D finite-strain model with the plane-strain condition is demonstrated to be well suited to accurately resolve the stress concentration during the lithiation process with significantly reduced computational cost.

For a comparative study, the electrochemical lithiation-delithiation behavior of individual *c*-GeNPs is studied with *in-situ* TEM. The results confirm that the lithiation of *c*-GeNPs involves a two-step phase transformation: c-Ge $\rightarrow a$ -Li_xGe $\rightarrow c$ -Li₁₅Ge₄, with a total volume expansion of ~260%, consistent with previous electrochemical tests. Fast multicycling of the GeNPs between the *a*-Ge and *a*-Li_xGe phases is demonstrated, with highly reversible expansion and contraction. In particular, the experimental results demonstrate that the *c*-GeNPs with a wide size range (from 100 nm to submicrometers) remained robust without fracture in multiple cycles, in distinct contrast to the sizedependent fracture of *c*-SiNPs upon the first lithiation. Based on the chemo-mechanical modeling, the lithiation anisotropy is demonstrated to cause the non-uniform stress in the hoop direction in lithiated *c*-SiNPs, leading to fracture in the well-defined planes. In the absence of such lithiation anisotropy, the *c*-GeNPs and *a*-SiNPs experience uniform hoop tension in the surface layer without the localized high stress and therefore remain robust throughout multicycling. In addition, the two-step lithiation in *a*-SiNPs can further alleviate the abruptness of the interface and hence the incompatible stress at the interface, leading to an even tougher behavior of *a*-SiNPs. Therefore, eliminating the lithiation anisotropy presents a novel pathway to mitigate the mechanical degradation in high-capacity electrode materials.

In addition to the study of retardation effect caused by lithiation self-generated internal stress, the influence of the external bending on the lithiation kinetics and deformation morphologies in GeNWs is also investigated. It is found that free-standing GeNWs undergo isotropic lithiation. Lithiation self-generated internal stress due to the incompatible strain at the reaction front causes lithiation retardation in the free-standing GeNWs, similar to SiNWs and SiNPs. Bending a GeNW during lithiation breaks the lithiation symmetry, enhancing the lithiation rate on the tensile side while suppressing it on the compressive side, both in the radial and the axial directions. The chemomechanical modeling corroborates the experimental observations and suggests the stress dependence of both Li diffusion and interfacial reaction rate during lithiation. The finding that external load can mediate lithiation kinetics opens new pathways to improve the performance of electrode materials by tailoring lithiation rate via strain engineering. Furthermore, in the light of bending-induced symmetry breaking of lithiation and considering a thin-film structure with pre-inserted secondary species (Li, hydrogen, sodium, etc.), bending of the thin film modifies the chemical potentials of the secondary species, leading to the flux of the inserted species from the compressive side to the tensile side. The mechanically controlled flux of the secondary species features a novel energy harvesting mechanism through mechanical stress.

Besides the continuum level chemo-mechanical modeling, MD simulations with the ReaxFF reactive force field are also conducted to investigate the fracture mechanisms of lithiation graphene. The simulation results show that the stress gradient around the crack tip drives the Li migration toward the crack tip, leading to the aggregation of Li around the crack tip. The aggregation of Li locally reduces the bond strength and subsequently the fracture strength on the one hand, and causes stress relaxation and reduction of the fracture driving force (and hence increase of the fracture strength) at the crack tip on the other. In the case of lithiated graphene, the former factor is dominant. Taking together of the stress-gradient driven Li migration and subsequent reduced fracture strength, lithiated graphene exhibits a self-weakening mechanism that causes the fracture of the graphene.

Moreover, systematic MD simulations are performed to identify two distinct fracture modes, abrupt and retarded fracture, in lithiated SWCNT containing two types of defects, single-vacancy and hole-like defect. Simulation results reveal that the defect size and Li concentration set the onset fracture strain, fracture strength, as well as the crack propagation speed. The relative time scales of crack propagation and Li diffusion dictate the fracture mode. Following the same argument, varying the loading rate can also control the fracture mode of the defective CNTs. The failure analysis of the defective CNTs upon lithiation, together with the cracked graphene, provides fundamental guidance to the lifetime extension of high capacity anode materials.

7.2 Future Work

The demand for high-capacity lithium-ion batteries (LIBs) for portable electronics, hybrid electric vehicles, and large scale energy storage has stimulated the relentless search for new electrode materials, and various anode materials have been identified as the promising candidates to replace current carbonaceous anodes in LIBs for their high theoretical capacity. However, rapid, irreversible capacity decay and poor cyclability, which arise largely due to the huge volume changes induced by Li insertion and extraction, remain a major technical barrier for commercializing high-capacity anodes such as Si and Ge. Therefore, a comprehensive understanding of the concurrent electro-chemo-mechanical processes during lithiation-delithiation cycling is necessary for the development of the next-generation high-density LIBs. Beyond the scope of this thesis, following questions remain interesting and are worthwhile to explore in future work.

Even though the chemo-mechanical model developed in this study can faithfully predict the lithiation-induced material behaviors observed in high capacity anodes by *insitu* TEM studies, the interfacial chemical reaction at reaction front is treated as diffusion for numerical convenience. As there is no length scale incorporated into the model, the size-dependent lithiation behaviors can not be captured by the current model. Therefore, it would be interesting to develop a real multiphysical reaction-diffusion model that couples with large elasto-plastic deformation, in which the interfacial chemical reaction is distinguished from bulk diffusion, and the thickness of the interfacial domain, as an intrinsic material length scale, is incorporated.

During the past few years, various continuum level chemo-mechanical models have been developed. However, systematic measurements of the material properties of electrodes are still lacking. Basic parameters, such as the modulus, Poison's ratio, yield strength, fracture energy, viscosity, diffusivity, and chemical reaction rate, which are dependent on not only the crystallographic orientations, but also the lithiation state, are needed to predict practical systems more faithfully.

Currently, most of the modeling works are focused on the first cycle lithiation. So far, very little attempt has been made to clarify the fatigue-caused failure mechanism of electrodes under multiple lithiation-delithiation cyclings. Therefore, new material constitutive laws need to be developed to mimic the behaviors of electrodes during multiple electrochemical cyclings. In addition, as lithium (Li) atoms are extracted from the anode materials during the delithiation process, nanosized voids will nucleate inside the electrodes. How the nanosized voids nucleate, grow, and finally lead to the failure of the electrodes is also worthwhile to study.

Although only a few anode materials are study herein, it would be also interesting to study Li insertion into other alloy anodes, such as tin (Sn), aluminum (Al), arsenic (As), etc. Previous study shows that doubling the capacity of the positive electrode (cathode) can increase the cell energy density by 57 percent, while increasing the capacity of the negative electrode (anode) by a factor of 10 can only lead to the increase of the overall cell energy density by 47 percent [6]. Therefore, new cathode materials are also needed to be explored [201].

Moreover, sodium-ion based electrochemical energy storage shows promise as a complementary alternative to the current lithium-ion based systems [202]. Due to the wide availability and low cost of sodium, sodium-based batteries possess the potential for meeting large scale grid energy storage needs. As sodium exhibits similar chemical properties as lithium, the knowledge developed for Li-ion batteries might be applied to ensure rapid progress in sodium-ion batteries.

Bibliography

- 1. Tarascon, J.M.; Armand, M., *Issues and challenges facing rechargeable lithium batteries*. Nature, 2001. **414**(6861): p. 359-367.
- 2. Winter, M.; Brodd, R.J., *What are batteries, fuel cells, and supercapacitors?* Chemical Reviews, 2004. **104**(10): p. 4245-4269.
- 3. Whittingham, M.S., *Materials challenges facing electrical energy storage*. Mrs Bulletin, 2008. **33**(4): p. 411-419.
- 4. Armand, M.; Tarascon, J.M., *Building better batteries*. Nature, 2008. **451**(7179): p. 652-657.
- 5. Takeuchi, E.S.; Leising, R.A., *Lithium batteries for biomedical applications*. Mrs Bulletin, 2002. **27**(8): p. 624-627.
- 6. Tarascon, J.M., *Key challenges in future Li-battery research*. Philosophical Transactions of the Royal Society A Mathematical Physical and Engineering Sciences, 2010. **368**(1923): p. 3227-3241.
- 7. Service, R.F., *Getting there*. Science, 2011. **332**(6037): p. 1494-1496.
- 8. Takada, K., *Progress and prospective of solid-state lithium batteries*. Acta Materialia, 2013. **61**(3): p. 759-770.
- 9. Marom, R.; Amalraj, S.F.; Leifer, N.; Jacob, D.; Aurbach, D., *A review of advanced and practical lithium battery materials*. Journal of Materials Chemistry, 2011. **21**(27): p. 9938-9954.
- Hayner, C.M.; Zhao, X.; Kung, H.H., *Materials for rechargeable lithium-ion batteries*. Annual Review of Chemical and Biomolecular Engineering, 2012. 3(1): p. 445-471.
- 11. Zhang, W.J., A review of the electrochemical performance of alloy anodes for *lithium-ion batteries*. Journal of Power Sources, 2011. **196**(1): p. 13-24.
- 12. Kamali, A.R.; Fray, D.J., *Review on carbon and silicon based materials as anode materials for lithium ion batteries*. Journal of New Materials for Electrochemical Systems, 2010. **13**(2): p. 147-160.
- 13. Neumann, G.; Würsig, A., *Lithium storage in silicon*. Physica Status Solidi Rapid Research Letters, 2010. **4**(1-2): p. A21-A23.
- 14. Beaulieu, L.Y.; Eberman, K.W.; Turner, R.L.; Krause, L.J.; Dahn, J.R., *Colossal reversible volume changes in lithium alloys*. Electrochemical and Solid State Letters, 2001. **4**(9): p. A137-A140.
- 15. Ryu, J.H.; Kim, J.W.; Sung, Y.-E.; Oh, S.M., *Failure modes of silicon powder negative electrode in lithium secondary batteries*. Electrochemical and Solid-State Letters, 2004. **7**(10): p. A306-A309.
- 16. Maranchi, J.P.; Hepp, A.F.; Evans, A.G.; Nuhfer, N.T.; Kumta, P.N., *Interfacial properties of the a-Si/Cu: active-inactive thin-film anode system for lithium-ion batteries.* Journal of the Electrochemical Society, 2006. **153**(6): p. A1246-A1253.

- Kasavajjula, U.; Wang, C.S.; Appleby, A.J., Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells. Journal of Power Sources, 2007. 163(2): p. 1003-1039.
- 18. Lee, S.W.; McDowell, M.T.; Choi, J.W.; Cui, Y., Anomalous shape changes of silicon nanopillars by electrochemical lithiation. Nano Letters, 2011. **11**(7): p. 3034-3039.
- Liu, X.H.; Zheng, H.; Zhong, L.; Huang, S.; Karki, K.; Zhang, L.Q.; Liu, Y.; Kushima, A.; Liang, W.T.; Wang, J.W.; Cho, J.-H.; Epstein, E.; Dayeh, S.A.; Picraux, S.T.; Zhu, T.; Li, J.; Sullivan, J.P.; Cumings, J.; Wang, C.; Mao, S.X.; Ye, Z.Z.; Zhang, S.; Huang, J.Y., *Anisotropic swelling and fracture of silicon nanowires during lithiation*. Nano Letters, 2011. **11**(8): p. 3312-3318.
- Lee, S.W.; McDowell, M.T.; Berla, L.A.; Nix, W.D.; Cui, Y., Fracture of crystalline silicon nanopillars during electrochemical lithium insertion. Proceedings of the National Academy of Sciences of the United States of America, 2012. 109(11): p. 4080-4085.
- 21. Linden, D.; Reddy, T., *Handbook of batteries*. 2001, McGraw-Hill Education, New York.
- Landi, B.J.; Ganter, M.J.; Cress, C.D.; DiLeo, R.A.; Raffaelle, R.P., *Carbon nanotubes for lithium ion batteries*. Energy & Environmental Science, 2009. 2(6): p. 638-654.
- 23. Larcher, D.; Beattie, S.; Morcrette, M.; Edstroem, K.; Jumas, J.C.; Tarascon, J.M., *Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries.* Journal of Materials Chemistry, 2007. **17**(36): p. 3759-3772.
- 24. Goldman, J.L.; Long, B.R.; Gewirth, A.A.; Nuzzo, R.G., *Strain anisotropies and self-limiting capacities in single-crystalline 3D silicon microstructures: models for high energy density lithium-ion battery anodes.* Advanced Functional Materials, 2011. **21**(13): p. 2412-2422.
- Cui, L.F.; Hu, L.B.; Choi, J.W.; Cui, Y., Light-weight free-standing carbon nanotube-silicon films for anodes of lithium ion batteries. Acs Nano, 2010. 4(7): p. 3671-3678.
- Huang, J.Y.; Zhong, L.; Wang, C.M.; Sullivan, J.P.; Xu, W.; Zhang, L.Q.; Mao, S.X.; Hudak, N.S.; Liu, X.H.; Subramanian, A.; Fan, H.; Qi, L.; Kushima, A.; Li, J., *In situ observation of the electrochemical lithiation of a single SnO₂ nanowire electrode*. Science, 2010. **330**(6010): p. 1515-1520.
- Chan, C.K.; Peng, H.L.; Liu, G.; McIlwrath, K.; Zhang, X.F.; Huggins, R.A.; Cui, Y., *High-performance lithium battery anodes using silicon nanowires*. Nature Nanotechnology, 2008. 3(1): p. 31-35.
- 28. Chan, C.K.; Zhang, X.F.; Cui, Y., *High capacity Li ion battery anodes using Ge nanowires*. Nano Letters, 2008. **8**(1): p. 307-309.
- 29. Rolison, D.R.; Nazar, L.F., *Electrochemical energy storage to power the 21st century*. Mrs Bulletin, 2011. **36**(7): p. 486-493.
- Liu, X.H.; Zhong, L.; Huang, S.; Mao, S.X.; Zhu, T.; Huang, J.Y., Size-dependent fracture of silicon nanoparticles during lithiation. Acs Nano, 2012. 6(2): p. 1522-1531.

- 31. Szczech, J.R.; Jin, S., *Nanostructured silicon for high capacity lithium battery anodes*. Energy & Environmental Science, 2011. **4**(1): p. 56-72.
- 32. Choi, N.S.; Yao, Y.; Cui, Y.; Cho, J., One dimensional Si/Sn based nanowires and nanotubes for lithium-ion energy storage materials. Journal of Materials Chemistry, 2011. **21**(27): p. 9825-9840.
- 33. Liu, X.H.; Zhang, L.Q.; Zhong, L.; Liu, Y.; Zheng, H.; Wang, J.W.; Cho, J.-H.; Dayeh, S.A.; Picraux, S.T.; Sullivan, J.P.; Mao, S.X.; Ye, Z.Z.; Huang, J.Y., Ultrafast electrochemical lithiation of individual Si nanowire anodes. Nano Letters, 2011. 11(6): p. 2251-2258.
- 34. Liu, N.; Hu, L.; McDowell, M.T.; Jackson, A.; Cui, Y., *Prelithiated silicon* nanowires as an anode for lithium ion batteries. Acs Nano, 2011. **5**(8): p. 6487-6493.
- 35. Liu, X.H.; Huang, S.; Picraux, S.T.; Li, J.; Zhu, T.; Huang, J.Y., *Reversible* nanopore formation in Ge nanowires during lithiation-delithiation cycling: an in situ transmission electron microscopy study. Nano Letters, 2011. **11**(9): p. 3991-3997.
- 36. Park, M.H.; Kim, M.G.; Joo, J.; Kim, K.; Kim, J.; Ahn, S.; Cui, Y.; Cho, J., *Silicon nanotube battery anodes*. Nano Letters, 2009. **9**(11): p. 3844-3847.
- Song, T.; Xia, J.; Lee, J.-H.; Lee, D.H.; Kwon, M.-S.; Choi, J.-M.; Wu, J.; Doo, S.K.; Chang, H.; Park, W.I.; Zang, D.S.; Kim, H.; Huang, Y.; Hwang, K.-C.; Rogers, J.A.; Paik, U., Arrays of sealed silicon nanotubes as anodes for lithium ion batteries. Nano Letters, 2010. 10(5): p. 1710-1716.
- Liu, Y.; Zheng, H.; Liu, X.H.; Huang, S.; Zhu, T.; Wang, J.; Kushima, A.; Hudak, N.S.; Huang, X.; Zhang, S.; Mao, S.X.; Qian, X.; Li, J.; Huang, J.Y., *Lithiationinduced embrittlement of multiwalled carbon nanotubes*. ACS Nano, 2011. 5(9): p. 7245-7253.
- 39. Maranchi, J.P.; Hepp, A.F.; Kumta, P.N., *High capacity, reversible silicon thin-film anodes for lithium-ion batteries*. Electrochemical and Solid-State Letters, 2003. **6**(9): p. A198-A201.
- 40. Nadimpalli, S.P.V.; Sethuraman, V.A.; Bucci, G.; Srinivasan, V.; Bower, A.F.; Guduru, P.R., *On plastic deformation and fracture in Si films during electrochemical lithiation/delithiation cycling*. Journal of the Electrochemical Society, 2013. **160**(10): p. A1885-A1893.
- 41. Choi, H.S.; Lee, J.G.; Lee, H.Y.; Kim, S.W.; Park, C.R., *Effects of surrounding* confinements of Si nanoparticles on Si-based anode performance for lithium ion batteries. Electrochimica Acta, 2010. **56**(2): p. 790-796.
- Ma, H.; Cheng, F.Y.; Chen, J.; Zhao, J.Z.; Li, C.S.; Tao, Z.L.; Liang, J., *Nest-like silicon nanospheres for high-capacity lithium storage*. Advanced Materials, 2007. 19(22): p. 4067-4070.
- 43. Yao, Y.; McDowell, M.T.; Ryu, I.; Wu, H.; Liu, N.; Hu, L.; Nix, W.D.; Cui, Y., *Interconnected silicon hollow nanospheres for lithium-ion battery anodes with long cycle life*. Nano Letters, 2011. **11**(7): p. 2949-2954.
- Liang, W.; Yang, H.; Fan, F.; Liu, Y.; Liu, X.H.; Huang, J.Y.; Zhu, T.; Zhang, S., *Tough germanium nanoparticles under electrochemical cycling*. Acs Nano, 2013. 7(4): p. 3427-3433.

- 45. Kim, H.; Cho, J., Superior lithium electroactive mesoporous Si@carbon coreshell nanowires for lithium battery anode material. Nano Letters, 2008. **8**(11): p. 3688-3691.
- 46. Huang, R.; Fan, X.; Shen, W.C.; Zhu, J., *Carbon-coated silicon nanowire array films for high-performance lithium-ion battery anodes*. Applied Physics Letters, 2009. **95**(13).
- 47. Cui, L.F.; Yang, Y.; Hsu, C.M.; Cui, Y., Carbon-silicon core-shell nanowires as high capacity electrode for lithium ion batteries. Nano Letters, 2009. **9**(9): p. 3370-3374.
- 48. Hertzberg, B.; Alexeev, A.; Yushin, G., *Deformations in Si-Li anodes upon electrochemical alloying in nano-confined space*. Journal of the American Chemical Society, 2010. **132**(25): p. 8548-8549.
- Wu, Z.S.; Ren, W.C.; Wen, L.; Gao, L.B.; Zhao, J.P.; Chen, Z.P.; Zhou, G.M.; Li, F.; Cheng, H.M., Graphene anchored with Co₃O₄ nanoparticles as anode of lithium ion batteries with enhanced reversible capacity and cyclic performance. Acs Nano, 2010. 4(6): p. 3187-3194.
- 50. Chen, H.X.; Dong, Z.X.; Fu, Y.P.; Yang, Y., *Silicon nanowires with and without carbon coating as anode materials for lithium-ion batteries.* Journal of Solid State Electrochemistry, 2010. **14**(10): p. 1829-1834.
- 51. Zhang, L.Q.; Liu, X.H.; Liu, Y.; Huang, S.; Zhu, T.; Gui, L.; Mao, S.X.; Ye, Z.Z.; Wang, C.M.; Sullivan, J.P.; Huang, J.Y., *Controlling the lithiation-induced strain and charging rate in nanowire electrodes by coating.* Acs Nano, 2011. **5**(6): p. 4800-4809.
- 52. Wu, H.; Chan, G.; Choi, J.W.; Ryu, I.; Yao, Y.; McDowell, M.T.; Lee, S.W.; Jackson, A.; Yang, Y.; Hu, L.B.; Cui, Y., *Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control.* Nature Nanotechnology, 2012. 7(5): p. 309-314.
- 53. Yi, R.; Dai, F.; Gordin, M.L.; Sohn, H.; Wang, D., *Influence of silicon nanoscale building blocks size and carbon coating on the performance of micro-sized Si-C composite Li-ion anodes*. Advanced Energy Materials, 2013. **3**(11): p. 1507-1515.
- 54. Sandu, G.; Brassart, L.; Gohy, J.-F.; Pardoen, T.; Melinte, S.; Vlad, A., *Surface coating mediated swelling and fracture of silicon nanowires during lithiation*. Acs Nano, 2014. **8**(9): p. 9427-9436.
- 55. Liu, X.H.; Wang, J.W.; Huang, S.; Fan, F.; Huang, X.; Liu, Y.; Krylyuk, S.; Yoo, J.; Dayeh, S.A.; Davydov, A.V.; Mao, S.X.; Picraux, S.T.; Zhang, S.; Li, J.; Zhu, T.; Huang, J.Y., *In situ atomic-scale imaging of electrochemical lithiation in silicon*. Nature Nanotechnology, 2012. 7(11): p. 749-756.
- 56. Liu, X.H.; Wang, J.W.; Liu, Y.; Zheng, H.; Kushima, A.; Huang, S.; Zhu, T.; Mao, S.X.; Li, J.; Zhang, S.; Lu, W.; Tour, J.M.; Huang, J.Y., *In situ transmission electron microscopy of electrochemical lithiation, delithiation and deformation of individual graphene nanoribbons.* Carbon, 2012. **50**(10): p. 3836-3844.
- 57. McDowell, M.T.; Lee, S.W.; Harris, J.T.; Korgel, B.A.; Wang, C.; Nix, W.D.; Cui, Y., *In situ TEM of two-phase lithiation of amorphous silicon nanospheres*. Nano Letters, 2013. **13**(2): p. 758-764.

- 58. Sun, C.-F.; Karki, K.; Jia, Z.; Liao, H.; Zhang, Y.; Li, T.; Qi, Y.; Cumings, J.; Rubloff, G.W.; Wang, Y., *A beaded-string silicon anode*. Acs Nano, 2013. 7(3): p. 2717-2724.
- 59. Wang, J.W.; He, Y.; Fan, F.; Liu, X.H.; Xia, S.; Liu, Y.; Harris, C.T.; Li, H.; Huang, J.Y.; Mao, S.X.; Zhu, T., *Two-phase electrochemical lithiation in amorphous silicon*. Nano Letters, 2013. **13**(2): p. 709-715.
- 60. Liu, X.H.; Huang, J.Y., *In situ TEM electrochemistry of anode materials in lithium ion batteries.* Energy & Environmental Science, 2011. **4**(10): p. 3844-3860.
- 61. Berla, L.A.; Lee, S.W.; Ryu, I.; Cui, Y.; Nix, W.D., *Robustness of amorphous silicon during the initial lithiation/delithiation cycle*. Journal of Power Sources, 2014. **258**(0): p. 253-259.
- 62. Liu, Y.; Liu, X.H.; Nguyen, B.-M.; Yoo, J.; Sullivan, J.P.; Picraux, S.T.; Huang, J.Y.; Dayeh, S.A., *Tailoring lithiation behavior by interface and bandgap engineering at the nanoscale*. Nano Letters, 2013. **13**(10): p. 4876-4883.
- 63. Limthongkul, P.; Jang, Y.-I.; Dudney, N.J.; Chiang, Y.-M., *Electrochemicallydriven solid-state amorphization in lithium-silicon alloys and implications for lithium storage.* Acta Materialia, 2003. **51**(4): p. 1103-1113.
- 64. Kang, K.; Lee, H.S.; Han, D.W.; Kim, G.S.; Lee, D.; Lee, G.; Kang, Y.M.; Jo, M.H., *Maximum Li storage in Si nanowires for the high capacity threedimensional Li-ion battery*. Applied Physics Letters, 2010. **96**(5).
- 65. McDowell, M.T.; Ryu, I.; Lee, S.W.; Wang, C.; Nix, W.D.; Cui, Y., *Studying the kinetics of crystalline silicon nanoparticle lithiation with in situ transmission electron microscopy*. Advanced Materials, 2012. **24**(45): p. 6034-6041.
- 66. Chon, M.J.; Sethuraman, V.A.; McCormick, A.; Srinivasan, V.; Guduru, P.R., *Real-time measurement of stress and damage evolution during initial lithiation of crystalline silicon.* Physical Review Letters, 2011. **107**(4): p. 045503.
- 67. Sethuraman, V.A.; Chon, M.J.; Shimshak, M.; Srinivasan, V.; Guduru, P.R., *In situ measurements of stress evolution in silicon thin films during electrochemical lithiation and delithiation*. Journal of Power Sources, 2010. **195**(15): p. 5062-5066.
- 68. Kubota, Y.; Escano, M.C.S.; Nakanishi, H.; Kasai, H., *Crystal and electronic structure of Li*₁₅*Si*₄. Journal of Applied Physics, 2007. **102**(5): p. 053704.
- 69. Kubota, Y.; Escano, M.C.S.; Nakanishi, H.; Kasai, H., *Electronic structure of LiSi*. Journal of Alloys and Compounds, 2008. **458**(1-2): p. 151-157.
- 70. Chevrier, V.L.; Dahn, J.R., *First principles model of amorphous silicon lithiation*. Journal of the Electrochemical Society, 2009. **156**(6): p. A454-A458.
- 71. Chevrier, V.L.; Dahn, J.R., *First principles studies of disordered lithiated silicon*. Journal of the Electrochemical Society, 2010. **157**(4): p. A392-A398.
- 72. Shenoy, V.B.; Johari, P.; Qi, Y., *Elastic softening of amorphous and crystalline Li-Si phases with increasing Li concentration: a first-principles study.* Journal of Power Sources, 2010. **195**(19): p. 6825-6830.
- 73. Zhang, Q.F.; Zhang, W.X.; Wan, W.H.; Cui, Y.; Wang, E.G., *Lithium insertion in silicon nanowires: an ab initio study.* Nano Letters, 2010. **10**(9): p. 3243-3249.

- 74. Wan, W.H.; Zhang, Q.F.; Cui, Y.; Wang, E.G., *First principles study of lithium insertion in bulk silicon.* Journal of Physics-Condensed Matter, 2010. **22**(41).
- 75. Zhang, Q.; Cui, Y.; Wang, E., Anisotropic lithium insertion behavior in silicon nanowires: binding energy, diffusion barrier, and strain effect. The Journal of Physical Chemistry C, 2011. **115**(19): p. 9376-9381.
- 76. Kim, H.; Kweon, K.E.; Chou, C.-Y.; Ekerdt, J.G.; Hwang, G.S., *On the nature and behavior of Li atoms in Si: a first principles study.* The Journal of Physical Chemistry C, 2010. **114**(41): p. 17942-17946.
- 77. Zhao, K.; Wang, W.L.; Gregoire, J.; Pharr, M.; Suo, Z.; Vlassak, J.J.; Kaxiras, E., *Lithium-assisted plastic deformation of silicon electrodes in lithium-ion batteries: a first-principles theoretical study.* Nano Letters, 2011. **11**(7): p. 2962-2967.
- 78. Chan, M.K.Y.; Long, B.R.; Gewirth, A.A.; Greeley, J.P., *The first-cycle electrochemical lithiation of crystalline Ge: dopant and orientation dependence and comparison with Si.* The Journal of Physical Chemistry Letters, 2011: p. 3092-3095.
- Stournara, M.E.; Guduru, P.R.; Shenoy, V.B., *Elastic behavior of crystalline Li-Sn phases with increasing Li concentration*. Journal of Power Sources, 2012. 208: p. 165-169.
- Meunier, V.; Kephart, J.; Roland, C.; Bernholc, J., *Ab initio investigations of lithium diffusion in carbon nanotube systems*. Physical Review Letters, 2002. 88(7): p. 075506.
- Fan, X.; Zheng, W.T.; Kuo, J.-L., Adsorption and diffusion of Li on pristine and defective graphene. ACS Applied Materials & Interfaces, 2012. 4(5): p. 2432-2438.
- 82. Zhou, L.-J.; Hou, Z.F.; Wu, L.-M., *First-principles study of lithium adsorption and diffusion on graphene with point defects.* The Journal of Physical Chemistry C, 2012. **116**(41): p. 21780-21787.
- 83. Garay-Tapia, A.M.; Romero, A.H.; Barone, V., *Lithium adsorption on graphene: from isolated adatoms to metallic sheets.* Journal of Chemical Theory and Computation, 2012. **8**(3): p. 1064-1071.
- Fan, X.; Zheng, W.T.; Kuo, J.-L.; Singh, D.J., Adsorption of single Li and the formation of small Li clusters on graphene for the anode of lithium-ion batteries. ACS Applied Materials & Interfaces, 2013. 5(16): p. 7793-7797.
- 85. Chou, C.-Y.; Kim, H.; Hwang, G.S., A comparative first-principles study of the structure, energetics, and properties of Li-M (M = Si, Ge, Sn) alloys. The Journal of Physical Chemistry C, 2011. **115**(40): p. 20018-20026.
- 86. Chan, M.K.Y.; Wolverton, C.; Greeley, J.P., *First principles simulations of the electrochemical lithiation and delithiation of faceted crystalline silicon*. Journal of the American Chemical Society, 2012. **134**(35): p. 14362-14374.
- 87. Cubuk, E.D.; Wang, W.L.; Zhao, K.; Vlassak, J.J.; Suo, Z.; Kaxiras, E., *Morphological evolution of Si nanowires upon lithiation: a first-principles multiscale model.* Nano Letters, 2013. **13**(5): p. 2011-2015.
- 88. Cubuk, E.D.; Kaxiras, E., *Theory of structural transformation in lithiated amorphous silicon*. Nano Letters, 2014. **14**(7): p. 4065-4070.

- Yang, H.; Huang, X.; Liang, W.; van Duin, A.C.T.; Raju, M.; Zhang, S., Selfweakening in lithiated graphene electrodes. Chemical Physics Letters, 2013. 563(0): p. 58-62.
- 90. Huang, X.; Yang, H.; Liang, W.; Raju, M.; Terrones, M.; Crespi, V.H.; van Duin, A.C.T.; Zhang, S., *Lithiation induced corrosive fracture in defective carbon nanotubes*. Applied Physics Letters, 2013. **103**(15): p. 153901-4.
- 91. Fan, F.F.; Huang, S.; Yang, H.; Raju, M.; Datta, D.; Shenoy, V.B.; van Duin, A.C.T.; Zhang, S.L.; Zhu, T., *Mechanical properties of amorphous Li_xSi alloys: a reactive force field study*. Modelling and Simulation in Materials Science and Engineering, 2013. 21(7): p. 074002.
- 92. Kim, S.P.; van Duin, A.C.T.; Shenoy, V.B., *Effect of electrolytes on the structure and evolution of the solid electrolyte interphase (SEI) in Li-ion batteries: a molecular dynamics study.* Journal of Power Sources, 2011. **196**(20): p. 8590-8597.
- 93. Kim, S.-P.; Datta, D.; Shenoy, V.B., *Atomistic mechanisms of phase boundary evolution during initial lithiation of crystalline silicon*. The Journal of Physical Chemistry C, 2014. **118**(31): p. 17247-17253.
- 94. Bower, A.F.; Guduru, P.R.; Sethuraman, V.A., *A finite strain model of stress, diffusion, plastic flow, and electrochemical reactions in a lithium-ion half-cell.* Journal of the Mechanics and Physics of Solids, 2011. **59**(4): p. 804-828.
- 95. Ryu, I.; Choi, J.W.; Cui, Y.; Nix, W.D., *Size-dependent fracture of Si nanowire battery anodes.* Journal of the Mechanics and Physics of Solids, 2011. **59**(9): p. 1717-1730.
- 96. Gao, Y.F.; Zhou, M., *Strong stress-enhanced diffusion in amorphous lithium alloy nanowire electrodes.* Journal of Applied Physics, 2011. **109**(1): p. 014310.
- 97. Haftbaradaran, H.; Song, J.; Curtin, W.A.; Gao, H., *Continuum and atomistic models of strongly coupled diffusion, stress, and solute concentration.* Journal of Power Sources, 2011. **196**(1): p. 361-370.
- 98. Zhao, K.J.; Pharr, M.; Vlassak, J.J.; Suo, Z.G., *Inelastic hosts as electrodes for high-capacity lithium-ion batteries*. Journal of Applied Physics, 2011. **109**(1): p. 016110.
- 99. Cui, Z.; Gao, F.; Qu, J., *A finite deformation stress-dependent chemical potential and its applications to lithium ion batteries.* Journal of the Mechanics and Physics of Solids, 2012. **60**(7): p. 1280-1295.
- Zhao, K.; Pharr, M.; Wan, Q.; Wang, W.L.; Kaxiras, E.; Vlassak, J.J.; Suo, Z., *Concurrent reaction and plasticity during initial lithiation of crystalline silicon in lithium-ion batteries.* Journal of the Electrochemical Society, 2012. 159(3): p. A238-A243.
- Pharr, M.; Zhao, K.; Wang, X.; Suo, Z.; Vlassak, J.J., *Kinetics of initial lithiation of crystalline silicon electrodes of lithium-ion batteries*. Nano Letters, 2012. 12(9): p. 5039-5047.
- Ryu, I.; Lee, S.W.; Gao, H.; Cui, Y.; Nix, W.D., *Microscopic model for fracture of crystalline Si nanopillars during lithiation*. Journal of Power Sources, 2014. 255(0): p. 274-282.

- 103. Cui, Z.; Gao, F.; Qu, J., *Interface-reaction controlled diffusion in binary solids with applications to lithiation of silicon in lithium-ion batteries.* Journal of the Mechanics and Physics of Solids, 2013. **61**(2): p. 293-310.
- 104. Huang, S.; Fan, F.; Li, J.; Zhang, S.; Zhu, T., *Stress generation during lithiation of high-capacity electrode particles in lithium ion batteries.* Acta Materialia, 2013. **61**(12): p. 4354-4364.
- 105. Arico, A.S.; Bruce, P.; Scrosati, B.; Tarascon, J.-M.; van Schalkwijk, W., *Nanostructured materials for advanced energy conversion and storage devices*. Nat Mater, 2005. **4**(5): p. 366-377.
- Bindumadhavan, K.; Srivastava, S.K.; Mahanty, S., *MoS2-MWCNT hybrids as a superior anode in lithium-ion batteries*. Chemical Communications, 2013. 49(18): p. 1823-1825.
- Courtel, F.; Duncan, H.; Abu-Lebdeh, Y., Beyond intercalation: nanoscaleenabled conversion anode materials for lithium-ion batteries, in Nanotechnology for Lithium-Ion Batteries, Abu-Lebdeh, Y., Davidson, I., Editors. 2013, Springer US. p. 85-116.
- Obrovac, M.N.; Christensen, L., *Structural changes in silicon anodes during lithium insertion/extraction*. Electrochemical and Solid State Letters, 2004. 7(5): p. A93-A96.
- 109. Cui, L.F.; Ruffo, R.; Chan, C.K.; Peng, H.L.; Cui, Y., *Crystalline-amorphous* core-shell silicon nanowires for high capacity and high current battery electrodes. Nano Letters, 2009. **9**(1): p. 491-495.
- 110. Magasinski, A.; Dixon, P.; Hertzberg, B.; Kvit, A.; Ayala, J.; Yushin, G., *Highperformance lithium-ion anodes using a hierarchical bottom-up approach*. Nature Materials, 2010. **9**(4): p. 353-358.
- 111. Scrosati, B.; Hassoun, J.; Sun, Y.K., *Lithium-ion batteries. A look into the future*. Energy & Environmental Science, 2011. **4**(9): p. 3287-3295.
- 112. Bruce, P.G.; Scrosati, B.; Tarascon, J.M., *Nanomaterials for rechargeable lithium batteries*. Angewandte Chemie-International Edition, 2008. **47**(16): p. 2930-2946.
- 113. Li, H.; Huang, X.J.; Chen, L.Q.; Wu, Z.G.; Liang, Y., *A high capacity nano-Si composite anode material for lithium rechargeable batteries*. Electrochemical and Solid State Letters, 1999. **2**(11): p. 547-549.
- 114. Yamada, M.; Ueda, A.; Matsumoto, K.; Ohzuku, T., *Silicon-based negative* electrode for high-capacity lithium-ion batteries: ``SiO''-carbon composite. Journal of the Electrochemical Society, 2011. **158**(4): p. A417-A421.
- 115. Liu, X.H.; Fan, F.; Yang, H.; Zhang, S.; Huang, J.Y.; Zhu, T., *Self-limiting lithiation in silicon nanowires*. Acs Nano, 2012. **7**(2): p. 1495-1503.
- 116. Newnham, R.E., *Properties of materials: anisotropy, symmetry, structure*. 2005, Oxford University Press, New York.
- 117. Wortman, J.J.; Evans, R.A., Young's modulus, shear modulus, and Poisson's ratio in silicon and germanium. Journal of Applied Physics, 1965. **36**(1): p. 153-156.
- 118. Yang, H.; Huang, S.; Huang, X.; Fan, F.; Liang, W.; Liu, X.H.; Chen, L.-Q.; Huang, J.Y.; Li, J.; Zhu, T.; Zhang, S., Orientation-dependent interfacial mobility governs the anisotropic swelling in lithiated silicon nanowires. Nano Letters, 2012. 12(4): p. 1953-1958.

- 119. ABAQUS, *Abaqus analysis user's manual*. Dassault Systemes, Providence, RI, USA, 2010.
- 120. Bower, A.F., Applied mechanics of solids. 2011: CRC Press, Boca Raton, FL.
- Bower, A.F.; Guduru, P.R., A simple finite element model of diffusion, finite deformation, plasticity and fracture in lithium ion insertion electrode materials. Modelling and Simulation in Materials Science and Engineering, 2012. 20(4): p. 045004.
- 122. Gao, Y.F.; Zhou, M., Strong dependency of lithium diffusion on mechanical constraints in high-capacity Li-ion battery electrodes. Acta Mechanica Sinica, 2012. **28**(4): p. 1068-1077.
- 123. Gao, Y.F.; Zhou, M., *Coupled mechano-diffusional driving forces for fracture in electrode materials.* Journal of Power Sources, 2013. **230**(0): p. 176-193.
- 124. Sethuraman, V.A.; Srinivasan, V.; Bower, A.F.; Guduru, P.R., *In situ measurements of stress-potential coupling in lithiated silicon*. Journal of the Electrochemical Society, 2010. **157**(11): p. A1253-A1261.
- 125. Haftbaradaran, H.; Gao, H.; Curtin, W.A., *A surface locking instability for atomic intercalation into a solid electrode*. Applied Physics Letters, 2010. **96**(9): p. 091909-3.
- 126. Grantab, R.; Shenoy, V.B., *Pressure-gradient dependent diffusion and crack propagation in lithiated silicon nanowires*. Journal of the Electrochemical Society, 2012. **159**(5): p. A584-A591.
- 127. Huggins, R.A.; Nix, W.D., Decrepitation model for capacity loss during cycling of alloys in rechargeable electrochemical systems. Ionics, 2000. **6**(1-2): p. 57-63.
- 128. He, Y.; Yu, X.; Li, G.; Wang, R.; Li, H.; Wang, Y.; Gao, H.; Huang, X., Shape evolution of patterned amorphous and polycrystalline silicon microarray thin film electrodes caused by lithium insertion and extraction. Journal of Power Sources, 2012. **216**(0): p. 131-138.
- 129. He, Y.; Yu, X.; Wang, Y.; Li, H.; Huang, X., Alumina-coated patterned amorphous silicon as the anode for a lithium-ion battery with high coulombic efficiency. Advanced Materials, 2011. **23**(42): p. 4938-4941.
- 130. Liu, X.H.; Liu, Y.; Kushima, A.; Zhang, S.; Zhu, T.; Li, J.; Huang, J.Y., *In situ TEM experiments of electrochemical lithiation and delithiation of individual nanostructures.* Advanced Energy Materials, 2012. **2**(7): p. 722-741.
- 131. Graetz, J.; Ahn, C.C.; Yazami, R.; Fultz, B., *Nanocrystalline and thin film germanium electrodes with high lithium capacity and high rate capabilities.* Journal of the Electrochemical Society, 2004. **151**(5): p. A698-A702.
- 132. Lee, H.; Kim, H.; Doo, S.-G.; Cho, J., *Synthesis and optimization of nanoparticle Ge confined in a carbon matrix for lithium battery anode material.* Journal of the Electrochemical Society, 2007. **154**(4): p. A343-A346.
- 133. Jo, G.; Choi, I.; Ahn, H.; Park, M.J., *Binder-free Ge nanoparticles-carbon hybrids for anode materials of advanced lithium batteries with high capacity and rate capability.* Chemical Communications, 2012. **48**(33): p. 3987-3989.
- 134. Xue, D.-J.; Xin, S.; Yan, Y.; Jiang, K.-C.; Yin, Y.-X.; Guo, Y.-G.; Wan, L.-J., Improving the electrode performance of Ge through Ge@C core-shell

nanoparticles and graphene networks. Journal of the American Chemical Society, 2012. **134**(5): p. 2512-2515.

- 135. Park, M.-H.; Cho, Y.; Kim, K.; Kim, J.; Liu, M.; Cho, J., *Germanium nanotubes prepared by using the kirkendall effect as anodes for high-rate lithium batteries.* Angewandte Chemie, 2011. **123**(41): p. 9821-9824.
- 136. Schwartz, B., *Chemical etching of germanium in the system* $HF-H_2O_2-H_2O$. Journal of the Electrochemical Society, 1967. **114**(3): p. 285-292.
- 137. Leancu, R.; Moldovan, N.; Csepregi, L.; Lang, W., *Anisotropic etching of germanium*. Sensors and Actuators A: Physical, 1995. **46**(1–3): p. 35-37.
- 138. Obrovac, M.N.; Krause, L.J., *Reversible cycling of crystalline silicon powder*. Journal of the Electrochemical Society, 2007. **154**(2): p. A103-A108.
- 139. Johnson, Q.; Smith, G.S.; Wood, D., *The crystal structure of Li*₁₅*Ge*₄. Acta Crystallographica, 1965. **18**(1): p. 131-132.
- 140. Wang, C.-M.; Li, X.; Wang, Z.; Xu, W.; Liu, J.; Gao, F.; Kovarik, L.; Zhang, J.-G.; Howe, J.; Burton, D.J.; Liu, Z.; Xiao, X.; Thevuthasan, S.; Baer, D.R., *In situ TEM investigation of congruent phase transition and structural evolution of nanostructured silicon/carbon anode for lithium ion batteries*. Nano Letters, 2012. 12(3): p. 1624-1632.
- 141. Liu, C.; Li, F.; Ma, L.P.; Cheng, H.M., *Advanced materials for energy storage*. Advanced Materials, 2010. **22**(8): p. E28-E62.
- 142. Cairns, E.J.; Albertus, P., Batteries for electric and hybrid-electric vehicles, in Annual Review of Chemical and Biomolecular Engineering, Vol 1, Prausnitz, J.M., Doherty, M.F., Segalman, M.A., Editors. 2010, Annual Reviews: Palo Alto. p. 299-320.
- 143. Liang, W.; Hong, L.; Yang, H.; Fan, F.; Liu, Y.; Li, H.; Li, J.; Huang, J.Y.; Chen, L.-Q.; Zhu, T.; Zhang, S., *Nanovoid formation and annihilation in gallium nanodroplets under lithiation-delithiation cycling*. Nano Letters, 2013. **13**(11): p. 5212-5217.
- 144. Klavetter, K.C.; Wood, S.M.; Lin, Y.-M.; Snider, J.L.; Davy, N.C.; Chockla, A.M.; Romanovicz, D.K.; Korgel, B.A.; Lee, J.-W.; Heller, A.; Mullins, C.B., A high-rate germanium-particle slurry cast Li-ion anode with high coulombic efficiency and long cycle life. Journal of Power Sources, 2013. **238**(0): p. 123-136.
- 145. Liu, Y.; Zhang, S.; Zhu, T., *Germanium-based electrode materials for lithium-ion batteries*. ChemElectroChem, 2014. **1**(4): p. 706-713.
- 146. Woo, S.-H.; Choi, S.J.; Park, J.-H.; Yoon, W.-S.; Hwang, S.W.; Whang, D., *Entangled germanium nanowires and graphite nanofibers for the anode of lithium-ion batteries.* Journal of the Electrochemical Society, 2013. **160**(1): p. A112-A116.
- 147. Gu, M.; Yang, H.; Perea, D.E.; Zhang, J.-G.; Zhang, S.; Wang, C.-M., Bendinginduced symmetry breaking of lithiation in germanium nanowires. Nano Letters, 2014. 14(8): p. 4622-4627.
- 148. McDowell, M.T.; Lee, S.W.; Nix, W.D.; Cui, Y., 25th anniversary article: understanding the lithiation of silicon and other alloying anodes for lithium-ion batteries. Advanced Materials, 2013. **25**(36): p. 4966-4985.

- 149. Roundy, D.; Cohen, M.L., *Ideal strength of diamond, Si, and Ge.* Physical Review B, 2001. **64**(21): p. 212103.
- 150. Smith, D.A.; Holmberg, V.C.; Korgel, B.A., *Flexible germanium nanowires: ideal strength, room temperature plasticity, and bendable semiconductor fabric.* Acs Nano, 2010. **4**(4): p. 2356-2362.
- 151. Yang, H.; Fan, F.; Liang, W.; Guo, X.; Zhu, T.; Zhang, S., *A chemo-mechanical model of lithiation in silicon*. Journal of the Mechanics and Physics of Solids, 2014. **70**(0): p. 349-361.
- 152. Dai, L.; Chang, D.W.; Baek, J.-B.; Lu, W., *Carbon nanomaterials for advanced energy conversion and storage*. Small, 2012. **8**(8): p. 1130-1166.
- 153. Centi, G.; Perathoner, S., *Carbon nanotubes for sustainable energy applications*. Chemsuschem, 2011. **4**(7): p. 913-925.
- 154. Pumera, M., *Graphene-based nanomaterials for energy storage*. Energy & Environmental Science, 2011. **4**(3): p. 668-674.
- 155. Hou, J.B.; Shao, Y.Y.; Ellis, M.W.; Moore, R.B.; Yi, B.L., *Graphene-based* electrochemical energy conversion and storage: fuel cells, supercapacitors and lithium ion batteries. Physical Chemistry Chemical Physics, 2011. **13**(34): p. 15384-15402.
- Brownson, D.A.C.; Kampouris, D.K.; Banks, C.E., An overview of graphene in energy production and storage applications. Journal of Power Sources, 2011. 196(11): p. 4873-4885.
- 157. Kaskhedikar, N.A.; Maier, J., *Lithium storage in carbon nanostructures*. Advanced Materials, 2009. **21**(25-26): p. 2664-2680.
- 158. de las Casas, C.; Li, W.Z., *A review of application of carbon nanotubes for lithium ion battery anode material.* Journal of Power Sources, 2012. **208**: p. 74-85.
- Wang, X.-L.; Han, W.-Q., Graphene enhances Li storage capacity of porous single-crystalline silicon nanowires. ACS Applied Materials & Interfaces, 2010. 2(12): p. 3709-3713.
- 160. Landi, B.J.; Cress, C.D.; Raffaelle, R.P., *High energy density lithium-ion batteries with carbon nanotube anodes*. Journal of Materials Research, 2010. **25**(8): p. 1636-1644.
- 161. Liang, M.; Zhi, L., *Graphene-based electrode materials for rechargeable lithium batteries*. Journal of Materials Chemistry, 2009. **19**(33): p. 5871-5878.
- 162. Bhardwaj, T.; Antic, A.; Pavan, B.; Barone, V.; Fahlman, B.D., *Enhanced electrochemical lithium storage by graphene nanoribbons*. Journal of the American Chemical Society, 2010. **132**(36): p. 12556-12558.
- 163. Chan, Y.; Hill, J.M., *Lithium ion storage between graphenes*. Nanoscale Research Letters, 2011. **6**: p. 203.
- Chen, J.; Minett, A.I.; Liu, Y.; Lynam, C.; Sherrell, P.; Wang, C.; Wallace, G.G., Direct growth of flexible carbon nanotube electrodes. Advanced Materials, 2008.
 20(3): p. 566-570.
- 165. Wang, G.; Shen, X.; Yao, J.; Park, J., *Graphene nanosheets for enhanced lithium storage in lithium ion batteries*. Carbon, 2009. **47**(8): p. 2049-2053.
- 166. Masarapu, C.; Subramanian, V.; Zhu, H.; Wei, B., Long-cycle electrochemical behavior of multiwall carbon nanotubes synthesized on stainless steel in Li ion batteries. Advanced Functional Materials, 2009. **19**(7): p. 1008-1014.
- 167. Pol, V.G.; Thackeray, M.M., *Spherical carbon particles and carbon nanotubes prepared by autogenic reactions: evaluation as anodes in lithium electrochemical cells.* Energy & Environmental Science, 2011. **4**(5): p. 1904-1912.
- 168. Mielke, S.L.; Troya, D.; Zhang, S.; Li, J.L.; Xiao, S.P.; Car, R.; Ruoff, R.S.; Schatz, G.C.; Belytschko, T., *The role of vacancy defects and holes in the fracture of carbon nanotubes*. Chemical Physics Letters, 2004. **390**(4-6): p. 413-420.
- 169. van Duin, A.C.T.; Dasgupta, S.; Lorant, F.; Goddard, W.A., *ReaxFF: a reactive force field for hydrocarbons.* Journal of Physical Chemistry A, 2001. **105**(41): p. 9396-9409.
- 170. Han, S.S.; van Duin, A.C.T.; Goddard, W.A.; Lee, H.M., *Optimization and application of lithium parameters for the reactive force field, ReaxFF.* Journal of Physical Chemistry A, 2005. **109**(20): p. 4575-4582.
- Russo, M.F.; van Duin, A.C.T., Atomistic-scale simulations of chemical reactions: bridging from quantum chemistry to engineering. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 2011. 269(14): p. 1549-1554.
- Huang, X.; Yang, H.; van Duin, A.C.T.; Hsia, K.J.; Zhang, S., Chemomechanics control of tearing paths in graphene. Physical Review B, 2012. 85(19): p. 195453.
- 173. Chenoweth, K.; Cheung, S.; van Duin, A.C.T.; Goddard, W.A.; Kober, E.M., *Simulations on the thermal decomposition of a poly(dimethylsiloxane) polymer* using the ReaxFF reactive force field. Journal of the American Chemical Society, 2005. **127**(19): p. 7192-7202.
- 174. Kubota, Y.; Ozawa, N.; Nakanishi, H.; Kasai, H., *Quantum states and diffusion of lithium atom motion on a graphene*. Journal of the Physical Society of Japan, 2010. **79**(1): p. 014601.
- 175. Chan, K.T.; Neaton, J.B.; Cohen, M.L., *First-principles study of metal adatom adsorption on graphene*. Physical Review B, 2008. **77**(23): p. 235430.
- 176. Zhang, S.; Zhu, T.; Belytschko, T., *Atomistic and multiscale analyses of brittle fracture in crystal lattices.* Physical Review B, 2007. **76**(9): p. 094114.
- 177. Terdalkar, S.S.; Huang, S.; Yuan, H.Y.; Rencis, J.J.; Zhu, T.; Zhang, S.L., *Nanoscale fracture in graphene*. Chemical Physics Letters, 2010. **494**(4-6): p. 218-222.
- Zhang, S.L.; Khare, R.; Lu, Q.; Belytschko, T., A bridging domain and strain computation method for coupled atomistic-continuum modelling of solids. International Journal for Numerical Methods in Engineering, 2007. 70(8): p. 913-933.
- 179. Pollak, E.; Geng, B.; Jeon, K.-J.; Lucas, I.T.; Richardson, T.J.; Wang, F.; Kostecki, R., *The interaction of Li⁺ with single-layer and few-layer graphene*. Nano Letters, 2010. **10**(9): p. 3386-3388.

- 180. Lee, E.; Persson, K.A., *Li absorption and intercalation in single layer graphene and few layer graphene by first principles.* Nano Letters, 2012. **12**(9): p. 4624-4628.
- 181. Shin, W.H.; Jeong, H.M.; Kim, B.G.; Kang, J.K.; Choi, J.W., *Nitrogen-doped multiwall carbon nanotubes for lithium storage with extremely high capacity*. Nano Letters, 2012. **12**(5): p. 2283-2288.
- 182. Chew, S.Y.; Ng, S.H.; Wang, J.; Novák, P.; Krumeich, F.; Chou, S.L.; Chen, J.; Liu, H.K., *Flexible free-standing carbon nanotube films for model lithium-ion batteries*. Carbon, 2009. **47**(13): p. 2976-2983.
- 183. Lahiri, I.; Oh, S.W.; Hwang, J.Y.; Cho, S.; Sun, Y.K.; Banerjee, R.; Choi, W., High capacity and excellent stability of lithium ion battery anode using interfacecontrolled binder-free multiwall carbon nanotubes grown on copper. Acs Nano, 2010. 4(6): p. 3440-3446.
- 184. Demczyk, B.G.; Wang, Y.M.; Cumings, J.; Hetman, M.; Han, W.; Zettl, A.; Ritchie, R.O., *Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes*. Materials Science and Engineering A, 2002. 334(1-2): p. 173-178.
- 185. Coleman, J.N.; Khan, U.; Blau, W.J.; Gun'ko, Y.K., *Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites.* Carbon, 2006. **44**(9): p. 1624-1652.
- 186. Shimoda, H.; Gao, B.; Tang, X.P.; Kleinhammes, A.; Fleming, L.; Wu, Y.; Zhou, O., Lithium intercalation into opened single-wall carbon nanotubes: storage capacity and electronic properties. Physical Review Letters, 2002. 88(1): p. 015502.
- 187. Khantha, M.; Cordero, N.A.; Alonso, J.A.; Cawkwell, M.; Girifalco, L.A., *Interaction and concerted diffusion of lithium in a (5,5) carbon nanotube*. Physical Review B, 2008. **78**(11): p. 115430.
- 188. Sun, J.; Liu, H.; Chen, X.; Evans, D.G.; Yang, W.; Duan, X., Carbon nanorings and their enhanced lithium storage properties. Advanced Materials, 2013. 25(8): p. 1125-1130.
- 189. Shin, H.-C.; Liu, M.; Sadanadan, B.; Rao, A., *Lithium insertion into chemically etched multi-walled carbon nanotubes*. Journal of Solid State Electrochemistry, 2004. 8(11): p. 908-913.
- 190. Eom, J.Y.; Kwon, H.S.; Liu, J.; Zhou, O., *Lithium insertion into purified and etched multi-walled carbon nanotubes synthesized on supported catalysts by thermal CVD.* Carbon, 2004. **42**(12–13): p. 2589-2596.
- 191. Eom, J.; Kim, D.; Kwon, H., *Effects of ball-milling on lithium insertion into multi-walled carbon nanotubes synthesized by thermal chemical vapour deposition.* Journal of Power Sources, 2006. **157**(1): p. 507-514.
- 192. Yang, S.; Song, H.; Chen, X.; Okotrub, A.V.; Bulusheva, L.G., *Electrochemical performance of arc-produced carbon nanotubes as anode material for lithium-ion batteries.* Electrochimica Acta, 2007. **52**(16): p. 5286-5293.
- 193. Chen, S.; Yeoh, W.; Liu, Q.; Wang, G., Chemical-free synthesis of graphenecarbon nanotube hybrid materials for reversible lithium storage in lithium-ion batteries. Carbon, 2012. **50**(12): p. 4557-4565.

- 194. Nishidate, K.; Hasegawa, M., *Energetics of lithium ion adsorption on defective carbon nanotubes.* Physical Review B, 2005. **71**(24): p. 245418.
- 195. Kar, T.; Pattanayak, J.; Scheiner, S., Insertion of lithium ions into carbon nanotubes: an ab initio study. The Journal of Physical Chemistry A, 2001. 105(45): p. 10397-10403.
- 196. Garau, C.; Frontera, A.; Quiñonero, D.; Costa, A.; Ballester, P.; Deyà, P.M., *Lithium diffusion in single-walled carbon nanotubes: a theoretical study.* Chemical Physics Letters, 2003. **374**(5-6): p. 548-555.
- 197. Zhao, M.; Xia, Y.; Mei, L., *Diffusion and condensation of lithium atoms in single-walled carbon nanotubes*. Physical Review B, 2005. **71**(16): p. 165413.
- 198. Sammalkorpi, M.; Krasheninnikov, A.; Kuronen, A.; Nordlund, K.; Kaski, K., *Mechanical properties of carbon nanotubes with vacancies and related defects*. Physical Review B, 2004. **70**(24): p. 245416.
- 199. Zhang, S.L.; Mielke, S.L.; Khare, R.; Troya, D.; Ruoff, R.S.; Schatz, G.C.; Belytschko, T., *Mechanics of defects in carbon nanotubes: atomistic and multiscale simulations.* Physical Review B, 2005. **71**(11).
- 200. Dumitrica, T.; Hua, M.; Yakobson, B.I., *Symmetry-, time-, and temperaturedependent strength of carbon nanotubes*. Proceedings of the National Academy of Sciences, 2006. **103**(16): p. 6105-6109.
- 201. Manthiram, A.; Fu, Y.; Su, Y.-S., *Challenges and prospects of lithium-sulfur batteries*. Accounts of Chemical Research, 2012. **46**(5): p. 1125-1134.
- 202. Slater, M.D.; Kim, D.; Lee, E.; Johnson, C.S., *Sodium-ion batteries*. Advanced Functional Materials, 2013. **23**(8): p. 947-958.

VITA

Hui Yang

Education

Ph.D., Engineering Science and Mechanics, 2014
The Pennsylvania State University, University Park, PA, USA
M.S., Engineering Mechanics, 2010
The Pennsylvania State University, University Park, PA, USA
B.S., Engineering Mechanics, 2006
Huazhong University of Science and Technology, Wuhan, Hubei, China

Publications

- 1. **Yang, H.**; Huang, S.; Huang, X.; Fan, F.; Liang, W.; Liu, X.H.; Chen, L.-Q.; Huang, J.Y.; Li, J.; Zhu, T.; Zhang, S., *Orientation-dependent interfacial mobility governs the anisotropic swelling in lithiated silicon nanowires.* Nano Letters, 2012. **12**(4): p. 1953-1958.
- 2. Liu, X.H.; Fan, F.; **Yang, H.**; Zhang, S.; Huang, J.Y.; Zhu, T., *Self-limiting lithiation in silicon nanowires*. Acs Nano, 2012. **7**(2): p. 1495-1503.
- 3. Huang, X.; Yang, H.; van Duin, A.C.T.; Hsia, K.J.; Zhang, S., *Chemomechanics* control of tearing paths in graphene. Physical Review B, 2012. **85**(19): p. 195453.
- Liang, W.; Yang, H.; Fan, F.; Liu, Y.; Liu, X.H.; Huang, J.Y.; Zhu, T.; Zhang, S., *Tough germanium nanoparticles under electrochemical cycling*. Acs Nano, 2013. 7(4): p. 3427-3433.
- Yang, H.; Huang, X.; Liang, W.; van Duin, A.C.T.; Raju, M.; Zhang, S., Selfweakening in lithiated graphene electrodes. Chemical Physics Letters, 2013. 563(0): p. 58-62.
- 6. Huang, X.; **Yang, H.**; Liang, W.; Raju, M.; Terrones, M.; Crespi, V.H.; van Duin, A.C.T.; Zhang, S., *Lithiation induced corrosive fracture in defective carbon nanotubes*. Applied Physics Letters, 2013. **103**(15): p. 153901-4.
- Liang, W.; Hong, L.; Yang, H.; Fan, F.; Liu, Y.; Li, H.; Li, J.; Huang, J.Y.; Chen, L.-Q.; Zhu, T.; Zhang, S., *Nanovoid formation and annihilation in gallium nanodroplets under lithiation–delithiation cycling*. Nano Letters, 2013. 13(11): p. 5212-5217.
- 8. Fan, F.F.; Huang, S.; **Yang, H.**; Raju, M.; Datta, D.; Shenoy, V.B.; van Duin, A.C.T.; Zhang, S.L.; Zhu, T., *Mechanical properties of amorphous LixSi alloys: a reactive force field study*. Modelling and Simulation in Materials Science and Engineering, 2013. **21**(7): p. 074002.
- 9. Gu, M.*; **Yang, H.***; Perea, D.E.; Zhang, J.-G.; Zhang, S.; Wang, C.-M., *Bending-induced symmetry breaking of lithiation in germanium nanowires*. Nano Letters, 2014. **14**(8): p. 4622-4627. (*Equal contributions)
- Yang, H.; Fan, F.; Liang, W.; Guo, X.; Zhu, T.; Zhang, S., A chemo-mechanical model of lithiation in silicon. Journal of the Mechanics and Physics of Solids, 2014. 70(0): p. 349-361.