IN SITU TEM STUDY ON ANODE MATERIALS IN LITHIUM-ION BATTERIES

A Dissertation in Engineering Science and Mechanics

by

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ABSTRACT

The growing demand for light-weight, high-capacity lithium-ion batteries (LIBs) for portable electronics, plug-in hybrid electric vehicles, and stationary energy storage systems has led to intensive research on developing new electrode materials with higher energy density, higher power density, and longer lifetime. However, a major issue with the high-capacity materials such as silicon (Si) is the rapid, irreversible capacity decay and poor cyclability due to the lithiation/delithiation induced mechanical degradation. A fundamental understanding of coupled electro-chemo-mechanical effects on the lithiation/delithiation of anode materials in LIBs is critical important for the development of advanced LIBs.

In this thesis, we constructed solid cell and liquid cell nanobatteries inside high-resolution transmission electron microscopy (HRTEM) for electrochemical tests and mechanical degradation study of anode materials in LIBs. With this approach, in situ TEM electrochemical tests of crystalline Si nanowires (SiNWs), germanium nanoparticles (GeNPs), SiNPs, and α-Fe₂O₃ nanowires have been performed. Integrating in situ TEM study with multiscale modeling, the failure mechanisms of these anode materials are characterized.

A set of interesting phenomena were discovered, ranging from ion and electron transport, electrochemical reactions, phase transformation, microstructural evolution, defect nucleation and growth, to chemo-mechanical failure inside battery materials. For SiNWs highly anisotropic swelling with huge volume expansion ~300% was observed upon first lithium insertion cycle. The highly anisotropic swelling was caused by the
much faster lithiation rate along <110> directions than the other directions. The anisotropy of lithiation induced stress concentration at the adjacent {110} planes, causing the formation of cracks and size-dependent fracture. The high compression stress at the lithiation front also causes retardation of lithiation.

A comparative study of electrochemical tests of GeNPs and SiNPs demonstrated that GeNPs exhibited tough lithiation/delithiation behavior without fracture in multiple cycles, in distinct contrast to the size-dependent fracture of crystalline SiNPs upon the first lithiation. GeNPs experienced large volume expansion similar to SiNPs, but showed isotropic lithiation behavior that differs to the highly anisotropic lithiation behavior of SiNPs. It turned out that lithiation anisotropy causes the non-uniform stress build-up in the hoop direction in lithiated SiNPs, leading to fracture in the well-defined planes.

During lithiation/delithiation cycles gallium nanodroplets (GaNDs) underwent reversible liquid-to-solid and amorphous to crystalline phase transitions. During delithiation, void nucleation, growth, and annihilation were observed, exhibiting a self-healing behavior. A phase field modeling and theoretical analysis unraveled the void growth and annihilation mechanisms as well as the associated time laws.

$\alpha$-Fe$_2$O$_3$ as a typical transition metal oxide is potential anode candidate for next generation LIBs. Inside in situ TEM, the high spatial resolution observation of lithiation of $\alpha$-Fe$_2$O$_3$ nanowires revealed the three-step lithiation process $\alpha$-Fe$_2$O$_3 \rightarrow \alpha$-LiFe$_2$O$_3 \rightarrow$ cubic-Li$_2$Fe$_2$O$_3 \rightarrow$ BCC-Fe with FCC-Li$_2$O. Our TEM results demonstrated the conversion reaction mechanism of lithiation in transition metal oxide electrodes.
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Chapter 1

Introduction

Advanced battery technologies are critically important for a wide range of applications, from portable electronics to plug-in hybrid electric vehicles and electric vehicles. They are also essential to the practical use of many types of renewable energy sources, such as solar and wind power, as stationary energy storage systems. Lithium ion batteries (LIBs) are presently the best performing advanced batteries, but they cannot meet requirements for more demanding applications due to limitations in capability and reliability. A variety of high capacity electrode materials have been identified, where silicon (Si) stands as the leading candidate with the highest theoretical capacity. However, these electrode materials suffer from serious capacity fading and poor cyclability due to the electrochemical lithiation/delithiation induced huge volume changes and mechanical degradation.

Recent studies on nanostructured Si electrodes suggested that tailoring the characteristic size of the electrodes may potentially mitigate Li$^+$ ion insertion induced mechanical degradation; thereby, opening a novel pathway for the design of mechanically reliable high-capacity electrodes. Currently, there is a lack of fundamental understanding of the stress generation and failure mechanisms in the lithiation process. Rational development of failure-resistant battery electrodes requires a fundamental understanding of the evolution of stress, deformation, damage, and electrochemistry in battery materials during cyclic charging and discharging. Therefore, a number of in situ techniques are
being developed including optical microscopy, X-ray diffraction (XRD),\textsuperscript{[38-40]} Raman spectroscopy,\textsuperscript{[41-43]} scanning electron microscopy (SEM),\textsuperscript{[44-47]} nuclear magnetic resonance (NMR) spectroscopy,\textsuperscript{[48-50]} as well as transmission electron microscopy (TEM)\textsuperscript{[51-54]} for battery studies. Among these techniques, \textit{in situ} TEM can provide high tempo-spatial resolution and the unique capability of microstructural characterization of electrodes during the electrochemical lithiation/delithiation process.\textsuperscript{[52,55-57]}

The objective of the thesis is to elucidate the mechanisms of electrochemically driven mechanical failures in the high-capacity electrodes of LIBs at the nanoscale by employing an \textit{in situ} TEM technique. In this thesis, we develop and use novel \textit{in situ} TEM experiments that allow real time investigation of morphological change, phase transformation, crack nucleation, and failure in nanoscale electrodes. The thesis work is primarily experimental, which was performed, in part, at the Sandia-Los Alamos Center for Integrated Nanotechnologies (CINT), a U.S Department of Energy, Office of Basic Energy Sciences user facility. Complementary multiscale computational studies coupling quantum mechanical simulations, atomistic simulations, and continuum-level finite element analysis are carried out through close collaborations within the research group of Professor Sulin Zhang at Penn State University and also the research group of Professor Ting Zhu at Georgia Institute of Technology, and the research group of Professor Long-Qing Chen at Penn State University. The integrated experimental-computational framework holds great promise in the design of next-generation high-efficiency LIBs.

This thesis is organized as follows. Chapter 2 introduces the lithium battery working principles, electrode materials of LIBs and the mechanics in lithiation/delithiation of LIB anode materials at nanoscale. Chapter 3 describes the \textit{in situ}
TEM technique in detail. Two types of experimental constructions so called “open cell” nanobatteries are introduced, which are liquid cell and solid cell. Liquid cell uses ionic liquid electrolyte and a small piece of bulk LiCoO₂ cathode. Differently, solid cell uses Li₂O/Li as the electrolyte and reference electrode. By using this in situ TEM technique, we perform real-time characterization of the electrochemical reaction inside the nanoscale electrodes. Chapter 4 studies the lithiation behavior of Si nanowires (SiNWs) during lithiation using the solid cell experimental configuration. Anisotropic swelling is observed in SiNW with <112> growth direction during electrochemical lithiation. The anisotropic deformation generates large stress concentration at the outer surface of the SiNWs, causing cracks and fracture. Chapter 5 reports the lithiation behavior of germanium nanoparticles (GeNPs) as the working electrodes in the in situ TEM solid cell. GeNPs show nearly isotropic expansion and extraction during electrochemical lithiation/delithiation cycling without forming any cracks and voids. These are distinctly different from the lithiation behavior of the SiNPs, which show anisotropic swelling and size-dependent fracture behavior with a critical size about 150nm, above which the particle will fracture and below which the particle will not. Chapter 6 explores lithiation/delithiation cycling behavior of the gallium nanodroplets (GaNDs). TEM studies observed the reversible liquid-to-solid phase transitions during lithiation and delithiation. A single nanovoid was observed to nucleate, grow, and annihilate during delithiation of GaNSs. The growth and annihilation time laws were also characterized. Chapter 7 studies the phase transformations of α-Fe₂O₃ during lithiation, where a conversion reaction mechanism with Li is revealed. Intermediate phases are found during the lithiation process, revealing three steps in the lithiation of α-Fe₂O₃ nanowires.
Chapter 2

Background

Conventional fossil-fuel energy resources including petroleum and coal have been playing a critically important role in the development of our modern world. Fossil-fuel energy is the material foundation of both increasing global economy and improving the quality of human life. Along with global population explosion and rapid economic growth, the need for energy supplies has been increasing dramatically.\textsuperscript{[58]} According to the international energy statistics data collected by the U.S. Energy Information Administration, the world total primary energy consumption in the year 2010 was increased nearly twice as much as that in the year 1980. The world total petroleum consumption increased from 63,119.9 thousand barrels per day in 1980 to 87,364.3 thousand barrels per day in 2010. In the mean time, we also have to face the fact that the huge amount of fossil fuel consumption also has effects on the natural environment. Such effects include global warming caused by increasing concentrations of CO\textsubscript{2} which are released by the burning of fossil fuels.\textsuperscript{[59]} Beside the green house effect, the utilization of fossil fuels also makes many kinds of pollutions to the earth where we live, such as air pollutions, water and land pollutions.\textsuperscript{[60]} Another very important issue is that fossil fuels are non-renewable resources and the reserves are finite. These very important facts have driven people to put significant efforts toward finding alternative energies to reduce the usage of fossil fuels and to meet the increasing demand of energy supply. Over the last several decades, the promising alternatives such as hydroelectric, nuclear, and renewable
have been experiencing more rapid development\cite{61-63} and has been playing more and more important role in our daily life. However, the amount of fossil fuels was still high, which is 80.6% of the total world energy consumption in 2010, as reported by REN21 Renewables 2012 Global Status Report. There is still a huge space to increase the usage of clean, renewable energy with higher efficiency.

Global warming and finite fossil-fuel supplies provide powerful incentives for the development of decarbonized forms of energy generation and storage.\cite{3, 5, 7-8} Batteries are electrochemical energy storage devices that can effectively convert stored chemical energy into electrical energy. They are currently being developed to provide energy for an increasingly diverse range of applications, from portable electronics to wireless power tools, from plug-in hybrid electric vehicles to all electric vehicles.\cite{10, 64-65} As shown in Figure 2.1,\footnote{4} among the present battery technologies, LIB is the best performing one owing to its high energy density, which exceeds any competing technologies by at least a factor of 2.5.\footnote{4} However, safety, cost, stored energy density, charge/discharge rates, and service life are issues that continue to prevent the LIB from meeting the requirements for the mass market, such as that of electric vehicles. Advanced battery technologies are critically needed.
2.1 Overview of Li-ion batteries

2.1.1 The working principles of lithium ion batteries

A battery is an energy storage device that converts chemical energy into electrical energy and consists of three main components: anode, cathode and electrolyte.\textsuperscript{[12]} LIBs are based on the intercalation/deintercalation reactions during which lithium is inserted into or extracted from both cathode and anode. In LIBs, the two electrodes are separated by an electrolyte. When the battery is being charged, the difference in the electrochemical
potentials of Li in the two electrodes drives Li ions (Li$^+$) to move from the positive (cathode) to negative (anode) electrode through the electrolyte. To maintain electrical neutrality, electrons flow from the positive to the negative through the electronic conductor. During discharge, the reverse occurs, and the chemical energy stored in the anode is transformed into electrical energy to power the working load.

As an example, Figure 2.2$^{[66-67]}$ schematically shows the working principles of the conventional Li-ion rechargeable battery comprised of a graphite anode, a non-aqueous liquid electrolyte, and a cathode of layered LiCoO$_2$. The cell potential is determined by the active materials cathode and anode in the cell. The electrochemical half-reaction (with charging being forward) in the positive electrode is:

$$
\text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-
$$

(2.1)

The other half-reaction in the negative electrode is

$$
x\text{Li}^+ + xe^- + 6\text{C} \leftrightarrow \text{Li}_x\text{C}_6
$$

(2.2)

The overall battery electrochemical reaction is

$$
\text{LiCoO}_2 + 6\text{C} \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}_6
$$

(2.3)

The change in the standard free energy $\Delta G^0$ of this reaction which is the driving force enabling a battery to deliver electrical energy to an external circuit is given by

$$
\Delta G^0 = -nFE^0
$$

(2.4)

where $n$ is the number of electrons transferred per mol of reactants, $F$ is the Faraday constant, and $E^0$ is the standard electromotive force of this reaction. When the cell is in the condition other than standard state, the voltage $E$ of a cell is calculated by the Nernst equation
\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_{Li_{1-x}CoO_2} a_{Li_xC_6}}{a_{LiCoO_2} a_C^{a}} \] (2.5)

where \( a_i \) is activity of relevant species, \( R \) is gas constant, and \( T \) is absolute temperature.

This equation provides the relationship between cell measurable cell voltage and the chemical difference across electrochemical cell reaction like (2.3).

In this type of LIB which is the most common commercial one in nowadays, during discharge, the lithium ions are extracted from the graphite layers, pass across the electrolyte, and are inserted into the layered LiCoO\(_2\) host. The transition metal Co in Li\(_x\)CoO\(_2\) is reduced from Co\(^{4+}\) to Co\(^{3+}\). The electrons pass around the external circuit. During charge, the exactly reverse process occurs. During the lithiation/delithiation process, the layer structure is maintained, resulting in good reversibility.

**Figure 2.2.** Schematic of a rechargeable LIB comprised of a negative electrode anode (graphite), a positive electrode cathode (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. Reprinted by permission from Royal Society of Chemistry [67], Copyright 2009
2.1.2 Electrode materials for Li-ion batteries

LIBs consist of lithium insertion compounds as both cathodes and anodes. They are also called as rocking-chair cells since the Li ion shuttles or rocks between the cathode and anode hosts during the charging/discharging process. The potential and capacity of the known lithium insertion compounds are shown in Figure 2.3.[4] The measures of the battery’s performance such as cell potential, capacity, and energy density are related to the intrinsic property of the chosen anode and cathode materials. The cycle-life and lifetime are dependent on the nature of the interface between the electrodes and electrolyte. The safety is a function of the stability of the electrode materials and interfaces. Construction of the high-performance batteries requires a careful selection of existing and new materials as negative (anode) and positive (cathode) electrodes, and appropriate electrolyte to minimize detrimental reactions associated with the electrode-electrolyte interface.
Figure 2.3. Voltage versus capacity for positive and negative electrode materials presently used or under serious considerations for the next generation of rechargeable Li-based cells.[4] Reprinted by permission from Nature [4], Copyright 2001

Four Li ion storage mechanisms for anode materials are intercalation/deintercalation, insertion/extraction, alloying/dealloying, and conversion reaction.[68] When Li ion is inserted into layer-structured anode materials, the host matrix structure usually has minimal structure evolution maintaining the layered structure. The conventional Graphite anode is one example of this type of materials.[69] The advantages are low-cost, good capacity retention, and very good cycle life. Its drawbacks are the low theoretical gravimetric capacity of 372 mAh/g, and volumetric capacity of 830mAh/ml. Insertion anode materials are similar to the layered intercalation ones. During lithiation, Li ions are inserted into the interstitials of the host material structures without changing the main structure of the host anode electrode such as Li₄Ti₅O₁₂.[70] Some elements such as Al,[71] Si,[24, 29, 35] Ge,[15, 72-74] Sn[75-76] can alloy with lithium and provide huge theoretical capacity ranging from 1000 to 4000 mAh/g. However, there is a large volume
change during lithiation/delithiation cycling, 300–400% for Li$_x$Si,$^{[17, 24]}$ 260-300% for Li$_x$Ge,$^{[72-73, 77]}$ and 260% for Li$_{4.4}$Sn.$^{[78]}$ Mechanical stresses induced by volume expansion lead to cracks and fracturing of the electrode, and eventual failure of the Li ion battery.$^{[24-25, 29]}$ The conversion anode materials refer to the transition metal oxides such FeO, Fe$_2$O$_3$, or CuO.$^{[68]}$ These materials have been found to have reversible conversion reaction with lithium recently.$^{[79-81]}$ The gravimetric capacity of transition metal oxides ranges from 650-1000mAh/g which is more than twice larger compared to graphite. They also are low-cost, environmentally benign and abundant. The drawback is that their potentials versus Li/Li$^+$ are higher than that of graphite as shown in Figure 2.4.$^{[68]}$

![Figure 2.4. Potential versus gravimetric capacity of anode materials.$^{[68]}$ Reprinted by permission from Springer [68], Copyright 2012](image)

**2.2 Mechanics in lithiation/delithiation of nanoscale anode materials**

To meet the increasing requirements for the demanding applications such as electric vehicles, plug-in hybrid electric vehicles, and stationary power storage for renewable energies like wind and solar energy, significant research over the last decade
has been directed towards finding materials with ever greater capacity to increase battery efficiency.\cite{1-8} According to the working principle of LIB, the capacity of the LIB largely depends on that of the anode to accommodate Li atoms. 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 anode to 372mAh/g, which is insufficient for high power applications. Compared to the Li-C anodes, a variety of Li-alloy (Li$_x$M, M = Sn, Si, Ge, Al)$^{15, 24, 29, 35, 71-76}$ anodes show substantially higher theoretical capacity, high Li packing density, and safe thermodynamic potential. For example, as the leading candidate for anode in LIBs, silicon has a theoretical capacity of 4200 mAh/g with the formation of Li$_{22}$Si$_5$ alloy at high temperature or 3579 mAh/g for Li$_{15}$Si$_4$ at room temperature.$^{24, 34, 50, 82}$ Unfortunately, mechanical degradation, as described below, has become a major obstacle for practical application of Si and other high capacity materials in rechargeable LIBs.$^{34, 36}$

Another issue is that the electrodes in the first-generation LIBs are composed of powders containing millimeter-sized particles, while the electrolyte is trapped within millimeter sized pores of a polypropylene separator. Because of the fairly low intrinsic diffusivity of the Li ion in the solid state,$^{83}$ the lithiation/delithiation rate, and hence charge/discharge rate, are limited, which results in the low-power. However, to meet the requirement for the future demands of hybrid electric vehicles and clean energy storage, an increase in the charging/discharging rate of LIBs of more than one order of magnitude is needed.
The inherent mechanical degradation of the high-capacity electrodes and low charging/discharging rate directed researchers to seek for solutions from nanotechnology.\cite{12,83-86} The advance of nanotechnology in the last decade enabled low-cost, fast fabrications of nanostructured materials with nanoscale controls on the size, shape, and chemical compositions. Nanomaterials because of their reduced dimensions can facilitate strain relaxation, enhance flaw tolerance, shorten Li and electron diffusion path, and increase surface area of the electrodes and thus have the great potential to make a significant impact on the performance of LIBs.\cite{13,15,17,21-22} A variety of nanostructures have been studied in order to explore the strategies of enabling the candidate electrode material such as Si to perform well. The size effect has been explored in a variety of Si nanostructures.\cite{29,87} Nanoelectrodes of different geometrical shapes were considered, including nanowires, nanotubes, thin films, and nanoparticles. Nanotube-like structures\cite{88-89} provide increased surface area accessible to the electrolyte, allowing Li ions to intercalate at both the interior and exterior of the nanotubes, and thereby increasing both the charging/discharging rate and the capacity. The increased surface area relieves stress build-up and facilitates the fast absorption of dislocations generated at the interior of the tube due to Li insertion, contributing the internal stress relaxation and mechanical stability.\cite{17,23,83} Despite some recent progresses, there is currently a critical lack of fundamental understanding of the electro-chemo-mechanical processes of Li insertion and extraction at the nanometer scale. In particular, the mechanisms of electro-chemically driven mechanical failures are little known. This has significantly plagued the development of Si-based electrodes with the extremely high charge capacity.
As we have mentioned, the mechanics of electrodes are critical in determining the performance and durability of LIBs. During battery charge-discharge cycling, lithium diffuses into and out of electrode crystallites, usually causing the crystallites to expand or contract. The volume change may lead to stresses and stress-induced degradation that can exhibit at several different length scales. Large volume expansions up to 300% occur in Si and Ge when they are fully lithiated, which can lead to particle decrepitation. Graphite, the most used negative electrode material, shows a volume expansion of up to 10%, but the associated stresses can still be high enough to cause particles to fracture, especially after cycling. Fractured graphite particles expose a fresh carbon surface to the electrolyte (this problem exists not only on graphite anodes, but also generally on other types of anodes), which leads to the formation of an additional solid electrolyte interface, resulting in capacity fading owing to a loss of available Li. In addition, expansion and contraction of electrode particles can cause particle rearrangement, which could lead to large contact stresses and fracture if the particles are sufficiently closely packed together. Figure 2.5 shows the fracture of lithiated Si thin film, resembling cracked mud in a dry lake bed. This mechanical degradation can cause the loss of electrical contact between active material (Si) and the current collector (metal substrate), leading to capacity fading and very poor cyclability. Si nanowires on the other hand can facilitate strain relaxation, maintain structure integrity after lithiation evidencing nanoscale electrodes are promising for advanced LIBs.
Figure 2.5. Mechanical degradation of Si electrodes. (a1) Schematic and (a2) experiment\(^{[13]}\) of morphological changes that occur in Si thin films during electrochemical cycling. 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. (b1) Schematic and (b2) experiment of electrochemical cycling of Si nanowires, from ref.\(^{[17]}\) 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. Reprinted by permission from Nature Nanotechnology \([17]\), Copyright 2008 and The Electrochemical Society \([13]\), Copyright 2001.

A number of theoretical and numerical models have recently been developed to address the coupling between Li diffusion and mechanical stress induced by lithiation/delithiation for understanding the consequent effects on fracture and failure.\(^{[28], [91-101]}\) While these models provided insight and guidance for the battery cell design and optimization, it is not clear regarding to the effective range and scope that the models can
be applied for material selection and design of nanostructured batteries. This arises mainly because of the lack of mechanistic understanding of the reaction and failure mechanisms in Li-alloys at the nanoscale, and the missing data regarding the real-time nanoscale degradation process of lithiation/delithiation electrodes. *In situ* TEM experimental studies on nanoscale anode electrodes in this thesis will shed light on the fundamental understanding and the development of failure-resistant high-performance electrodes.
Chapter 3

In situ TEM experimental procedures

To study the mechanical deformation, morphology evolution, and phase transformation during electrochemical cycling of nanoscale LIB electrodes, *in situ* TEM was performed in this thesis. Two types of nanoscale batteries one a so called “liquid cell” and the other a “solid cell” were constructed inside the TEM. The TEM enables one to observe the electrochemical reaction in real time. The liquid cell has a similar construction to the real battery consisting of a single nanowire as anode, an ionic liquid electrolyte (ILE), and a piece of bulk LiCoO$_2$ as cathode. Differently, the solid cell is a half-cell using a single nanowire or nanoparticle as the working electrode, Li$_2$O/Li as the solid-state electrolyte and reference electrode.

3.1 Overview of *in situ* TEM

TEM/HRTEM is a very efficient approach to study the structure and properties of matter in material science.$^{102}$ Because of developments in electron microscopic techniques, the most advanced TEM nowadays can provide a spatial resolution as high as 50pm. In this same time, a variety of advanced TEM sample holders have been fabricated, which enable real-time visualization when specimen are under different loading conditions, such as: applied electric field,$^{103}$ elevated temperatures,$^{104}$ cryogenic environment,$^{105}$ and mechanical load.$^{106}$ This progress opens new pathways
for the characterization of material structures and properties using \textit{in situ} TEM (up to atomic scale).

\textit{In situ} TEM has been extensively used in materials science to perform mechanical and electrical property tests, and crystal structures characterizations, because of its high spatial resolution. Liu et al.\cite{107} reported \textit{in situ} TEM electrical measurements of polytypic silver nanowires. Jin et al.\cite{108} constructed new nanotube structures using two carbon nanotubes inside a TEM. Kodambaka et al.\cite{109} studied the Ge nanowire growth that occurred below the eutectic temperature using \textit{in situ} TEM. Huang et al.\cite{110} reported the super-plasticity of carbon nanotubes under elevated temperature condition.

\textit{In situ} TEM has recently been explored for battery research.\cite{52, 55-56, 111-112} The electrolytes for conventional LIBs usually are liquid which are not compatible with the high vacuum TEM column. To realize \textit{in situ} TEM observations of electrochemical reaction inside LIBs, liquid cells by sealing liquid electrolytes from high vacuum with electron transparent silicon nitride membrane windows for imaging have been constructed.\cite{111, 113} The biggest advantage of this design is that the configuration of the liquid cell and electrolyte could be the same as the real LIBs, so that reaction information from liquid cells could be used directly to provide guidance for the design of the real LIB. The disadvantages of liquid cells include poor image quality and limited spatial resolution due to the thick liquid layer, risk of leakage and damaging the TEM vacuum, and difficulty to perform analytical TEM techniques.

In this thesis, a new \textit{in situ} TEM technique called “open cell” nanobattery is applied,\cite{52} which is different from sealed liquid cell discussed above. The open cell batteries have two types of configurations liquid cell and solid cell. Liquid cell uses
nanowires as anode materials, bulk LiCoO$_2$ as cathode, and ILE (ionic liquid electrolyte) as the electrolyte, which has an ultra low vapor pressure$^{[114]}$ compatible with the high vacuum of TEM. The solid cell is a half-cell consisting of single nanowires or nanoparticles as the working electrodes, with Li$_2$O/Li as solid state electrolyte and a reference electrode.$^{[53-54]}$ The advantages of “open cell” are obvious and include real time and atomic scale resolution microstructure investigation, and concurrent nanometer to atomic scale composition analysis. Analytical TEM techniques such as electron diffraction patterns (EDPs), electron energy loss spectroscopy (EELS), and energy dispersive X-ray spectroscopy (EDS) could be performed for crystal structure, electronic structure and chemical information analysis.

3.2 in situ TEM instruments

3.2.1 The TEM-STM system: TEM holders for in situ STM and electrical probing

In this thesis, a Nanofactory Holder as the TEM-STM (Transmission Electron Microscopy-Scanning Tunneling Microscopy)$^{[115]}$ platform was used to setup the nanobatteries. Figure 3.1 shows the photos of a TEM-STM platform including the control unit, the TEM-STM holder compatible with FEI TEM and the zoom-in view of the head of the holder. The TEM-STM system provides a unique combination of TEM and STM techniques, which are used simultaneously in one instrument for the full sample characterization. The TEM-STM system consists of a STM equipped TEM sample holder, a controller, and a PC with Nanofactory’s data acquisition software. There are
two parts in the head of the holder. One part is a movement controlling part called the STM unit, and the other part is the sample holder. The movement is driven by a piezo tube with a ball on the top. By the six metal legs, a copper octopus-like hat with a STM probe can clamp on the ball. By controlling the piezo tube, the STM probe can move along the mutual-orthogonal axes X, Y and Z in the TEM. The samples which are Pt or Al rods with nanowires or nanoparticles working electrodes attached on one end in the experiments are fixed on the sample holder side by a small copper screw.

Figure 3.1. Schematic of a Nanofactory TEM-STM platform. (a) The control unit of the TEM-STM platform. (b) Side view of a TEM-STM holder compatible with FEI TEM. (c) Zoom-in view of the head of the holder. [116]
3.2.2 The control software of TEM-STM platform

The software Nanofactory Instruments 3 (NF3) is used to control the movement of the piezo and record the outputs such as force with displacement or current with bias. Figure 3.2 shows the interface of the NF3. As shown in Figure 3.2, the movement controller can both coarsely (Coarse movement part of Movement window in Figure 3.2) and finely control (Fine movement part of Movement window in Figure 3.2) the movement of the STM probe or the sample along the three directions: back-forward, up-down, and left-right. The fine movement has a resolution of 0.001 nm. The TEM-STM system has a wide variety of applications. It can be used for measuring the electrical properties at specific locations of the nanostructure with sub-nanometer accuracy. It can also measure the contact current and modulate the bias which is essential for the in situ battery study.

Figure 3.2. Interface of the software Nanofactory Instruments 3 and the interface of the Movement Controller.
3.3 Fabrication of nanobatteries

3.3.1 Liquid cell

As shown in Figure 3.3, the liquid cell consists of SiNWs as anode, ILE as the electrolyte, and a small piece of bulk LiCoO$_2$ as cathode with the electron beam going through the SiNWs for observation. In a typical experimental setup, SiNWs with Si wafer were glued on an Al or Pt rod using silver epoxy. One drop of the ILE was placed on surface of the LiCoO$_2$ bulk, and the LiCoO$_2$ bulk was glued to an Al rod with silver epoxy. The ILE was essentially a molten salt, which was made by dissolving the lithium salt LiTFSI in a solvent of P$_1$4TFSI at a concentration of 10wt% LiTFSI (LiTFSI: lithium bis(trifluoromethylsulfonyl) imide, P$_1$4TFSI: 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide).[114]

The liquid cell can be regarded as a miniaturized LIB at nanoscale. It is called an “open cell” because this nanoscale LIB is assembled inside the TEM without packaging, leaving it to the vacuum. It is noted that the electron beam could induce degradation of the ILE. During the experiments, a critical electron dose about $10^3$ A/cm$^2$ was found below which the ILE could survive a long time. At strong electron beam intensity, the ILE was solidified quickly and lost the capability of Li$^+$ transport. Another issue is that, by using this liquid cell, it is hard to conduct electrochemical tests for nanoparticles or short nanowires due to the small sizes of objects, which could be absorbed into the liquid electrolyte.
Figure 3.3. Schematic illustration of the *in situ* TEM liquid cell. SiNWs on the Si wafer were attached on the edge of the Al rod, serving as anode electrode. ILE was the electrolyte and a bulk LiCoO$_2$ was cathode electrode. Using the piezomanipulator, the ILE was driven to immerse the selected SiNW. Lithiation experiments were conducted by applying a negative potential on the working electrode with respect to the counter electrode.

3.3.2 Solid cell

The *in situ* TEM solid cell consists of a single nanowire/nanoparticle as the working electrode, Li metal as the reference electrode, and the Li$_2$O layer on the Li metal as a solid electrolyte as shown in Figure 3.4. A small (which was big enough for a nanobattery test) piece of Li metal was scratched with a tungsten tip inside a glove box filled with Ar to make the reference electrode. Then the holder with Li metal was loaded into TEM with exposure time to the air less than 2 seconds. The Li metal served as reference electrode and lithium source, and the naturally-grown Li$_2$O layer on the Li metal served as the solid-state electrolyte for Li$^+$ transport. During lithiation, a negative bias -2 V was applied to the working electrode with respect to the Li metal reference.
electrode. Li$_2$O has a band gap up to $\sim8eV$\cite{117} indicating that it is an electronic insulator. The electrochemical cycling experiment results in this thesis also demonstrated that Li$_2$O is indeed Li$^+$ conductor at nanoscale.\cite{72}

Although Li$_2$O is not usually used as electrolyte in conventional LIBs, a solid cell could be used for fundamental studies of lithiation/delithiation behavior of nanowires or nanoparticles. Compared to the liquid cell, the whole nanowire or nanoparticle is visible in the electrochemical process, offering complete microstructural information from very beginning of lithiation or delithiation in a solid cell. Another benefit of using solid cell is that atomic scale lithiation process could be observed due to the all solid configuration with minimal sample movement.

The electron beam effect on the solid cell is e-beam decomposition of Li$_2$O.\cite{118-119} Strong e-beam doses could decompose Li$_2$O directly to Li and O$_2$, which could induce chemical lithiation of working electrode without applying any potential.

Figure 3.4. Schematic illustration of the in situ TEM solid cell. SiNWs on the Si wafer were attached on the edge of the Al rod, serving as working electrode. The Li metal on the W tip served as reference electrode and lithium source, and the naturally-grown Li$_2$O layer on the Li metal served as the solid-state electrolyte for Li$^+$ transport. Using the piezomanipulator, the Li$_2$O/Li electrode was driven to contact the selected SiNW. Lithiation experiments were conducted by applying a negative potential on the working electrode with respect to the counter electrode.
Chapter 4

*In Situ* TEM Study of Lithiation Behavior of Si Nanowires

In this chapter, the phase transformation and morphology evolution in a single SiNW during electrochemical lithiation/delithiation were studied with *in situ* TEM by using a solid cell that was introduced in last chapter. The cell consisted of a single SiNW working electrode, a Li$_2$O solid electrolyte and bulk Li reference electrode. Upon lithiation, a reaction front propagated along the nanowire, causing the surface of the nanowire to swell due to the formation of an amorphous Li$_x$Si phase, which then crystallized into a Li$_{15}$Si$_4$ shell, leaving an unlithiated crystalline Si core. The volume expansion was highly anisotropic, the expansion occurred predominately along the radial <110> directions (~170% increase in diameter) with less than 20% diameter extension in the transverse <111> directions. This highly anisotropic expansion resulted in a dumbbell-shaped cross-section, which is attributed to plastic flow of the shell and a necking instability. Driven by the progressive lithiation of the Si core and expansion of the lithiated shell, the stress concentration at the neck region led to cracking, eventually splitting the single nanowire into two symmetrical sub-wires. These results provide mechanistic insights into electrochemically induced microstructural evolution and have implications for designing high energy density electrodes in advanced LIBs.
4.1 Introduction

The demand for light-weight, high-capacity LIBs for portable electronics, plug-in hybrid electric vehicles, and large-scale energy storage has led to intense, continual search over the last decade on new electrode materials with ever higher energy density.\textsuperscript{[1-8]} Si possesses the highest electrochemical energy capacity among all materials (4200mAh/g for Li_{22}Si_{5}, 3579mAh/g for Li_{15}Si_{4}), over an order of magnitude higher than that of the graphite used in current LIBs. However, Si experiences a 300% volume expansion after full lithiation, and the large volume change during cycling causes fracture and pulverization, leading to capacity fading.\textsuperscript{[13-14, 17, 28, 34, 82, 120-122]} How cracks initiate and evolve during cycling remains unclear. A fundamental understanding of the plastic deformation and fracture mechanisms in lithiated Si may help develop strategies to mitigate the large expansion and crack formation during cycling, thus paving the way for the application of Si as a high energy density anode in LIBs.\textsuperscript{[51, 123]} In this chapter, a nanoscale all-solid electrochemical cell was constructed inside a TEM consisting of a single SiNW, Li_{2}O/Li solid electrolyte/reference electrode enabling real time observations of the structure evolution of electrodes during electrochemical reactions.

4.2 Experimental approach

SiNWs were synthesized by VLS (vapor-liquid-solid) growth from Au catalyst islands on Si substrate. The \textit{n}-type SiNWs were grown by passing 250 standard cubic centimeters (sccm) of silane (SiH_{4}, 50% diluted with argon) and 100 sccm of phosphine (PH_{3}, 100 ppm) at a pressure of 3 Torr across a Si substrate containing Au catalyst
particles. The deposition temperature and time was 510 °C and 30 minutes. The P/Si ratio was $1.0 \times 10^{-4}$. Figure 4.1 shows the typical pristine SiNW with $<112>$ growth direction. A twin boundary between $T_1$ and $T_2$ (Figure 4.1a) is parallel to the [111] plane as indicated by the contrast in Figure 4.1a and EDP in Figure 4.1b. From the HRTEM image of Si, we see an oxidation layer about 2 nm covering on the surface of the nanowire.

![Figure 4.1](image)

**Figure 4.1.** The microstructure of a pristine SiNW. (a) Low magnification image of SiNW with diameter about 200nm. (b) The EPD of the SiNW along the zone axis [110]. (c) HRTEM image of SiNW with SiO$_x$ layer.

Figure 4.2 shows the schematic illustration of the experimental setup. Lithium metal was loaded as the Li source and reference electrode, while a naturally-grown Li$_2$O layer on the surface of the Li metal served as the solid electrolyte for Li$^+$ transport. SiNWs on Si substrate were affixed to an Al rod and then fixed on the sample holder end. Li$_2$O/Li counter electrode was translated via piezom manipulator to contact with selected
SiNWs and then a potential of -2V was applied to the SiNW with respect to the Li counter electrode to initiate the lithiation of SiNW.

![Schematic illustration of the in situ TEM experimental setup. SiNWs were attached on the edge of the Al rod, serving as working electrode. Li$_2$O layer on the Li metal served as the solid-state electrolyte for Li$^+$ transport. Li metal was the reference electrode. Lithiation experiments were conducted by applying a negative potential on the working electrode with respect to the counter electrode.](image)

**Figure 4.2.** Schematic illustration of the *in situ* TEM experimental setup. SiNWs were attached on the edge of the Al rod, serving as working electrode. Li$_2$O layer on the Li metal served as the solid-state electrolyte for Li$^+$ transport. Li metal was the reference electrode. Lithiation experiments were conducted by applying a negative potential on the working electrode with respect to the counter electrode.

### 4.3 Crack formation during lithiation of SiNWs

After the tip of the SiNW contacted with Li$_2$O, a bias of -2V was applied to the SiNW with a diameter of 216nm as shown in Figure 4.3a, and lithiation initiated at the Au cap, leading to its elongation (Figure 4.3b). Lithiation then occurred in the SiNW (Figure 4.3b), and a reaction front (marked by red arrows) in Figure 4.3b-i propagated progressively along the longitudinal axis of the nanowire. In the meantime, lithiation also occurred along the radial direction, from the surface to the core, leading to the formation of a thick shell with an unlithiated crystalline Si(c-Si) core. The c-Si core exhibited a tapering shape, with its diameter shrinking continuously from the reaction front towards the point of initial contact. Surprisingly, at the point the c-Si core disappeared (when the
Si was fully lithiated, a nanocrack formed (Figure 4.3e). This crack continued to grow as the lithiation front progressed further along the wire. Within about 200s, the crack grew from 260 nm to 1640 nm during the fast stage of lithiation (Figure 4.3e-g), but then growth stopped as the lithiation reaction slowed down (Figure 4.3g-i).

**Figure 4.3.** Crack formation and propagation in the center of a SiNW during lithiation. Arrows point out the reaction fronts. (a) Pristine SiNW with diameter 216nm contacting Li₂O/Li. (b-d) Lithiation via a core-shell manner. As the reaction front propagated towards the nanowire base, lithiation proceeded from the surfaces towards the center of the nanowire. A c-Si core was visible at this stage. Note that the Au cap was deformed/lithiated. (f-j) Crack evolution in the center of the nanowire. The length of the crack increased quickly in the initial stage, but finally stayed at 1760nm.
Figure 4.4 shows a more detailed structural characterization of the same lithiated SiNW as in Figure 4.3. A very large diameter change was observed along this viewing direction, an increase from 216 nm for the pristine SiNW (Figure 4.4a) to 580 nm (Figure 4.4b) with an obvious crack 200 nm in the center of the nanowire. The EDP from the lithiated segment of the nanowire confirmed the formation of a polycrystalline Li$_{15}$Si$_4$ (c-Li$_{15}$Si$_4$) phase mixed with amorphous Li$_x$Si ($a$-Li$_x$Si) (Figure 4.4c), consistent with previous reports.$^{[38, 40, 124-125]}$

**Figure 4.4.** Structural characterization of the lithiated and cracked SiNW. (a) Straight pristine Si nanowire with a uniform diameter of 216 nm and a semispherical gold cap. (b) Crack in the center of the nanowire after lithiation. The diameter of the nanowire expanded to 580nm along the vertical direction, with a maximum crack width of 200 nm. (c) EDP showing the formation of polycrystalline Li$_{15}$Si$_4$ and amorphous Li$_x$Si alloy after lithiation.

To further analyze the crack in lithiated SiNW, a scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) image was taken. In Figure 4.5b the STEM-HAADF image with Z-contrast (Z is atomic number) shows a crack near
the right end of the nanowire which is the dark contrast indicating less mass in this region. The unreacted core near the reaction front to the left end of the crack shown in Figure 4.5a was consistent with Figure 4.5b showing c-Si core with the bright Z-contrast. Figure 4.5c shows an electron energy loss spectroscopy (EELS) map of Li, confirming the presence of Li in the lithiated shell of the nanowire. Figure 4.5d-e show line scans across the crack (red line in Figure 4.5b, d) and the partially lithiated part (green line in Figure 4.5b, e) of the nanowire, respectively. The crack was revealed by an intensity dip in both the Z-contrast intensity (black line in Figure 4.5d) and the Si-Kα (1.7 keV) energy-dispersive X-ray spectroscopy (EDX) intensity (red trace in Figure 4.5d). In contrast, Figure 4.5e indicates that average Z was significantly lower in the lithiated Li_{15}Si_{4} shell than the unlithiated c-Si core.
4.4 Anisotropic swelling of SiNW during lithiation

The large diameter change observed in Figure 4.4a-b would correspond to a volume expansion of over 600% if a cylindrical shape of the nanowire before and after charging was assumed, in contradiction to the expected theoretical value of 281% volume...
expansion using bulk densities for Si and Li$_{15}$Si$_4$. To understand the anomalous expansion, it is critical to know the exact cross-sectional shape of the nanowire before and after charging. The real cross-section shape was resolved when the Li$_{15}$Si$_4$ nanowire was bent and viewed along different angles (Figure 4.6a), revealing a unique dumbbell shape for the cross-section of the nanowire. A series of images taken at different tilts revealed the dumbbell morphology of the lithiated nanowire (Figure 4.6a), which is in contrast to the circular cross-section of the pristine nanowires (Figure 4.6b). Figures 4.6c-i show that the lithiated nanowire exhibits less volume expansion when viewed along the [1\bar{1}0] zone axis. The pristine SiNW had very uniform diameter and a twin boundary parallel to the axis (Figure 4.6c, d). The EDP confirmed the following orthogonal directions: [112] was the growth direction; [1\bar{1}1] was the norm of the twin boundary; and [1\bar{1}0] was the electron beam incident direction (Figure 4.6d, e). Viewed from this direction, lithiation of the nanowire revealed only a 17% diameter expansion, from the original 155 nm to 180 nm (Figure 4.6f-h). However, tilting of the lithiated nanowire to a viewing direction closer to [1\bar{1}1] showed an obvious crack in the center of the nanowire (Figure 4.6j), and also a much larger expansion (from the original 155 nm to 485 nm) (Figure 4.6i). Observations on other nanowires confirmed the same anisotropic expansion: the diameter expands by ~170% along <1\bar{1}0> but less than 20% along <111> directions.
Figure 4.6. Anisotropic volume expansion of SiNW during lithiation. (a-b) Tilting series images showing cross-sections of a lithiated and a pristine SiNW, respectively, showing the cross-section changed from the initial circular shape (b) to a dumbbell shape after lithiation (a). (c) Pristine straight SiNW with uniform diameter. (d) Higher magnification image of the pristine SiNW with a visible twin boundary in the middle. (e) EDP showing the twin viewed along the [1̅1̅0] zone axis. The growth direction of the nanowire was [112], and the twin boundary was parallel to (11̅1). (f-h) Lithiation of the SiNW. The visible diameter expansion was only 17% and no elongation was observed. The red arrows mark the longitudinal reaction fronts. (i-j) Lithiated nanowire in (h) viewed along [1̅1̅0]_{Si} and close to [11̅1]_{Si} directions, respectively, showing the anisotropic volume expansion.
The anisotropic swelling of SiNW during lithiation is highly possible because of anisotropic lithium diffusion along different directions of c-SiNW. The physical origin of such large diffusion anisotropy for Li is not well understood, but it is expected to be controlled by interfacial processes. We note that similar interface-mediated anisotropic responses have been widely observed in both oxidation and wet etching of c-Si.\textsuperscript{126-128} Understanding its mechanistic basis requires a systematic study of lithiation reactions, accounting for factors such as the interfacial reactive layer,\textsuperscript{128} the bond density and states near the interface,\textsuperscript{126} and stress effects on reaction and diffusivity.\textsuperscript{129} This anisotropic response can also be similarly governed by the interfacial reaction, assuming the lithiation is limited by the interfacial reaction propagation speed. Yang et al.\textsuperscript{130} in professor Sulin Zhang’s group have established a chemo-mechanical model and simulation results have confirmed that the lithiation process is controlled by the movements of reaction front rather than the Li diffusion and the anisotropic swelling origins from the anisotropic interfacial mobility as shown in Figure 4.7. The progressive lithiation can readily cause the buildup of high stresses, leading to plastic deformation. In Figure 4.4b, the formation of surface cracks was observed at the cross section with full lithiation, where the Si core just disappeared. To explain this fracture mode, we note that the present necking instability is driven by the internal expansion associated with lithiation of the Si core. Because of the absence of the external load and constraint, the resultant force at any plane of the wire has to be zero, such that both the tensile and compressive stresses must coexist. The stress is tensile near the surface indent and compressive in the Si core. The former tends to drive the growth of the neck and facilitate the initiation of a surface crack, while the latter resists this crack initiation. As lithiation
proceeds, the c-Si core is reduced, leading to diminishment of the region of compressive stress. The vanishing region of compressive stress near the center of the wire allows the unstable growth of the indent that progresses to form cracks.

![Figure 4.7. Lithium flux profiles and morphologies of lithiated SiNWs at a representative lithiation snapshot for all the four SiNWs, showing that the dominate flux in the <110> directions, a direct consequence of high reactivity of Li at the {110} phase boundary.](image)

Our detailed microstructural observations lead to several important implications for the development of Si anode materials for LIBs. First, lithiation of crystalline Si leads to highly anisotropic Li$_{15}$Si$_4$ product formation which can promote cracking, but this process could be mitigated. For example, orienting the nanowires along a <110> crystallographic axis could promote wire lengthening as the primary volume expansion mechanism. Second, if conductive coatings are applied to the surface of the nanowires, these coatings are more likely to remain intact along the {111} surfaces of the nanowire, as the expansion is lower in the <111> directions. Third, the use of amorphous Si as an anode material would likely remove the anisotropy associated with initial lithiation and could suppress cracking.
4.5 Summary

The morphology changes associated with initial lithiation have been identified by using real time in situ TEM observations of the lithiation of SiNWs. It was revealed that the large volume expansion as Si converts to Li$_{15}$Si$_4$ occurs in a highly anisotropic fashion in free-standing nanowires of $<112>$ growth directions, resulting in an intermediate dumbbell-shaped wire cross-section. Despite extensive plastic flow of the lithiation product, very large stresses may nonetheless be developed inside the nanowire, which can lead to cracking of the nanowire and fracture. The anisotropic swelling of Si upon lithiation provides guidance for design of advanced LIBs using Si electrodes.
Chapter 5

In Situ TEM study of Ge and Si Nanoparticles under Electrochemical Cycling

Mechanical degradation of the electrode materials during electrochemical cycling remains a serious issue that critically limits the capacity retention and cyclability of rechargeable LIBs. In this chapter, we studied the highly reversible expansion and contraction of germanium nanoparticles (GeNPs), and anisotropic expansion and fracture of silicon nanoparticles (SiNPs) under lithiation-delithiation cycling with in situ TEM. During multiple cycles to the full capacity, the GeNPs remained robust without any visible cracking despite ~260% volume changes, in contrast to the size dependent fracture of SiNPs upon the first lithiation. The comparative in situ TEM study of fragile silicon nanoparticles suggests that the tough behavior of GeNPs can be attributed to the weak anisotropy of the lithiation strain at the reaction front. The tough germanium nanoparticles offer substantial potential for the development of durable, high-capacity and high-rate anodes for advanced LIBs.

5.1 Introduction

The development of advanced LIBs requires new electrode materials with superior energy density, power density and cyclability.\cite{2, 4, 6} Mechanical degradation of these electrode materials during electrochemical cycling remains a serious issue\cite{13, 24-25, 28-29, 31-32, 131} that critically limits the cycle life of LIBs. Silicon (Si) is being considered as
the next-generation anode material due to its high Li capacity (3579 mAh\(^{-1}\)),\(^{[34]}\) more than an order of magnitude higher than the carbonaceous materials (372 mAh\(^{-1}\)) currently used in LIBs. However, during electrochemical lithiation, Si electrodes undergo large and anisotropic expansion up to \(\sim 280\%\), leading to fracture and capacity loss even in the first cycle.\(^{[13, 24-25, 28-29, 31-32, 131]}\) Germanium (Ge), a group IV element as carbon and Si, has thus far received less attention. Several unique characteristics position Ge as a promising anode material. It possesses a high capacity (1384 mAh\(^{-1}\)).\(^{[124]}\) Both the electronic conductivity of Ge and the Li diffusivity within Ge are much higher than those in Si,\(^{[15-16]}\) thereby enabling the high-rate performance of Ge electrodes. Despite these favorable properties and recent experiments showing the high performance of Ge-based anodes,\(^{[132-135]}\) the capacity retention and cyclability of Ge electrodes, which are major concerns for high-capacity anodes, remain unclear.

Here in this chapter, the highly reversible expansion and contraction of GeNPs, and anisotropic expansion and fracture of SiNPs have been studied under electrochemical cycling using \textit{in situ} TEM. The results revealed that during multiple lithiation-delithiation cycles GeNPs of a large size range (from 100nm to submicron) remained robust without any visible cracking despite \(\sim 260\%\) volume changes. This is in stark contrast to the size dependent fracture of SiNPs upon the first lithiation.\(^{[29]}\) To reveal the strong crystallographic orientation effect on fracture in fragile SiNPs the further \textit{in situ} TEM study was conducted and supported by the chemomechanical modeling. On this basis we attribute the tough behavior of GeNPs to the weak anisotropy of the lithiation strain at the reaction front (\textit{i.e.}, the phase boundary between the amorphous shell and crystalline core), which correlates with its nearly crystallographic orientation-independent
mobility.\cite{57, 73, 136-137} The lithiation isotropy mitigates the buildup of high, non-uniform stresses, presenting a novel mechanism of averting the fracture in high-capacity electrodes.

5.2 Experimental approach

GeNPs were prepared by grinding a Ge wafer for about 30 minutes. The ground Ge powders were then dispersed in ethanol solution, followed by ultrasonic treatment. A tip-flattened Pt rod was dipped into the solution with Ge powders. GeNPs were attached onto the end of the Pt rod because of surface interaction. Figure 5.1 shows typical pristine GeNPs with nearly spherical shape. The diameters of these as-prepared GeNPs range from submicron to ~150 nm (620nm, 240nm, and 150nm shown in Figure 5.1a, c, and d respectively). The electron diffraction pattern (EDP) in Figure 5.1b and insets in Figure 5.1c, d indicated that the as-prepared GeNPs were single crystalline, denoted as $c$-GeNP. Figure 5.2 shows another pristine GeNP with diameter ~160 nm. The EDP in Figure 5.2b and high-resolution TEM image indicated the GeNP was a single crystal and covered by a 2 nm thick oxidation layer GeO$_x$.

SiNPs used in our experiments were a commercialized product of US Research Nanomaterials, Inc. The Si powders were dispersed in ethanol solution, followed by ultrasonic treatment. A tip-flattened Pt rod was dipped into the solution. SiNPs were attached onto the end of the Pt rod because of surface interaction. Figure 5.3 shows typical pristine SiNPs with a spherical shape. The diameters of these SiNPs ranged from ~1500 nm to ~150 nm. The EDP in Figure 5.3e taken from a group of SiNPs indicated
that the SiNPs were crystalline, rather than amorphous phase, denoted as c-SiNP. Figure 5.3f shows EDP from an individual SiNP indicated this SiNP was single crystalline with zone axis [111].

**Figure 5.1.** The typical TEM images and EDPs of as-prepared GeNPs with nearly spherical shape. The GeNPs are on the side surface of Pt rod. (a-b) A GeNP with diameter of 620nm and the EDP showing the crystalline phase. (c) A GeNP with diameter of 240nm. The inset is the corresponding EDP. (d) A GeNP with diameter of 150nm. The inset is the corresponding EDP.
Figure 5.2. Microstructure of a single crystalline GeNP. (a) The GeNP size is about 160nm in diameter with nearly spherical shape. (b) The EDP confirms the single crystalline phase. (c) HRTEM image shows that a ~2nm amorphous oxide layer on the surface.

Figure 5.3. The typical TEM images and EDPs of SiNPs with spherical shape. (a-d) Morphology of pristine SiNPs with diameter of 1360nm, 612nm, 310nm, and 154nm respectively. (e) EDP taken from a group of SiNPs indicates the crystalline phase. (f) EDP taken from an individual SiNP shows the single crystalline phase.
To study the lithiation-delithiation cycling behavior of Ge/SiNPs, an electrochemical device suited for *in situ* TEM experiment was constructed, as schematically shown in Figure 5.4. The device consisted of three essential components: a single Ge/SiNP as the working electrode sitting on a Pt rod, a small piece of bulk Li metal as the counter electrode, and a native Li$_2$O surface layer on the Li metal as the solid electrolyte. All the electrochemical tests were conducted in a Tecnai F-30 HRTEM with a Nanofactory TEM-scanning tunneling microscopy (STM) holder. The *in situ* TEM study enables the real-time imaging of electrochemical reactions during the lithiation-delithiation cycling. [24, 35, 52, 73, 138-139]

![Figure 5.4. Schematic illustration of the *in situ* nanobattery setup, consisting of a single GeNP/SiNP as the working electrode, bulk Li metal as the counter electrode, and a naturally grown Li$_2$O surface layer as the solid electrolyte.](image)

### 5.3 Lithiation-delithiation results of GeNPs

Figure 5.5 shows the morphological evolution and phase transformation of an individual nearly spherical shaped $c$-GeNP (diameter ~620 nm). To initiate the lithiation, a bias potential of -2V was applied to the $c$-GeNP with respect to a Li metal reference
electrode. The entire surface of the GeNP was quickly covered by Li\(^+\) ions, due to their much higher diffusion rate on the surface than in the bulk of Ge, similar to Si\(^{29}\). At 106s (Figure 5.5b), the GeNP began to expand, indicative of the start of bulk lithiation. As the lithiation proceeded (see Figure 5.5c), Li flowed nearly uniformly from the surface to the center of the GeNP along the radial direction, forming the structure with a core of c-Ge and a lithiated shell of amorphous Li\(_x\)Ge (a-Li\(_x\)Ge). A similar core-shell mode of lithiation was also observed in crystalline Si nanowires (c-SiNWs)\(^{24, 35}\) and c-SiNPs\(^{29}\) shown next in this chapter. Figure 5.5c shows that the lithiated GeNP expanded in a nearly isotropic manner to 830nm. The isotropy of lithiation can be clearly seen from the approximately uniform thickness of the amorphous shell, where the core-shell interface is directed by the red arrow (Figure 5.5c). At 632s, the GeNP was fully lithiated (Figure 5.5d) and its diameter increased to 946 nm, which corresponds to \(~260\%\) volume increase, consistent with the \(~280\%\) volume increase of the fully lithiated SiNPs (a-Li\(_{15}\)Si\(_4\))\(^{29, 125}\) shown next in this chapter. The lithiated GeNP consisted of the a-Li\(_{15}\)Ge\(_4\) phase, which was subsequently crystallized to c-Li\(_{15}\)Ge\(_4\)\(^{140-141}\) as identified by the EDP in Figure 5.5f. The crystallization of a-Li\(_x\)Ge to c-Li\(_{15}\)Ge\(_4\) was a simultaneous process for the whole nanoparticle without any phase boundary observed, which is similar to the congruent crystallization of a-Li\(_x\)Si\(^{141}\). The two-step phase transformation of c-Ge \(\rightarrow\) a-Li\(_x\)Ge \(\rightarrow\) c-Li\(_{15}\)Ge\(_4\) is consistent with the previous study of lithiation in c-GeNWs\(^{73}\). However, the lithiated GeNP did not fracture even though its initial size was considerably large, in contrast to the c-SiNPs that typically fracture into pieces upon lithiation provided that the initial diameter exceeds \(~150\text{nm}\)\(^{29}\).
Figure 5.6 shows the lithiation behavior of another GeNP with a nearly ellipsoidal shape. The major and minor axes of the ellipsoidal GeNP were 272nm and 197nm, respectively, as shown in Figure 5.6a. The GeNP was identified as $c$-Ge by EDP (Figure 5.6g). The Li$_2$O/Li electrolyte and reference electrode was relatively thick, as observed from the dark contrast of Li$_2$O/Li in Figure 5.6b, which provided as a strong confinement to the expansion of the GeNP along the vertical direction in the image plane upon lithiation. After a bias of -2V potential was applied, Li propagated from the surface to the core of the GeNP gradually. The reaction fronts are labeled by the red arrows at 147 s and 199s in Figure 5.6c and d. At 355s the $c$-GeNP was nearly fully lithiated to $a$-Li$_x$Ge (Figure 5.6e) and shortly the $a$-Li$_x$Ge was crystallized to $c$-Li$_{15}$Ge$_4$ (Figure 5.6f). The volume of the $a$-Li$_x$Ge phase in Figure 5.6e was almost the same as that of the $c$-Li$_{15}$Ge$_4$ phase, indicating that $x$ is fairly close to 3.75 in the $a$-Li$_x$Ge phase. Again fracture did not occur in this GeNP during the lithiation process. In the fully lithiated stage, the major axis of the ellipsoidal GeNP elongated from 272nm to 442nm while the minor axis from 197nm to 236nm. It is worth noting that the apparent larger expansion in the major axis than in the minor axis was due to the strong confinement of the thick Li$_2$O/Li electrode, rather than the orientation-dependent reaction rate that explains the anisotropic swelling in lithiated Si. This behavior of shape evolution of GeNP during lithiation also indicates that GeNP is easy to relax the stress generated by lithiation without forming cracks like SiNP.
Figure 5.5. Morphological evolution and phase transformation in a c-GeNP during lithiation. (a) A pristine c-GeNP with a diameter of ~ 620 nm with crystalline phase indentified by EDP in (e). (b-d) TEM snapshots showing the morphological evolution and uniform volume expansion of the GeNP upon lithiation. (b) A pristine GeNP was brought into contact with the Li$_2$O/Li electrode. (c) 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. (d) The c-Li$_{15}$Ge$_4$ phase formed after full lithiation to a-Li$_{15}$Ge$_4$, as indicated by the EDP shown in (f).
Figure 5.6. Electrochemical lithiation of an ellipsoid-shaped Ge nanoparticle. (a) The initial state of the Ge nanoparticle which is polycrystalline characterized by EDP (g). This Ge nanoparticle has a length about 272 nm in one dimension and about 197 nm in the other dimension. (b-e) The lithiation starts from the surface of the Ge nanoparticle since a thin amorphous layer is observed first after the -2V is applied. It induces elongation in both dimensions. The intermediate phase Li$_x$Ge alloy is formed. (f) The amorphous phase Li$_x$Ge is crystallized to c-Li$_{15}$Ge$_4$ which is confirmed by the EDP(h).
The cycling behavior of GeNPs was examined next. A \( a \)-GeNP with a nearly spherical shape and initial diameter of \(~160\text{nm}\) was selected, as shown in Figure 5.7a. The corresponding EDP is given in Figure 5.7b, confirming its single-crystalline phase. A bias of \(-1\text{V}\) was applied to this GeNP. After \(54\text{s}\) the \( a \)-GeNP was fully lithiated to \( a \)-\( \text{Li}_{15}\text{Ge}_4 \) (Figure 5.7c), and its diameter increased to \(247\ \text{nm}\), corresponding to \(~260\%\) volume increase. Then the potential was reversed to \(+1\text{V}\) before crystallization occurred. The spherical \( a \)-\( \text{Li},\text{Ge} \) NP shrunk instantly in a uniform manner and was fully delithiated to its original size \(\sim 160\ \text{nm}\) (Figure 5.7d), which suggested that the \(\text{Li}^+\) ions had been completely extracted from the \( a \)-\( \text{Li}_{15}\text{Ge}_4 \) NP. The fully delithiated phase was identified as \( a \)-Ge, as examined in detail later. After the first cycle, repeated lithiation-delithiation between \( a \)-Ge and \( a \)-\( \text{Li},\text{Ge} \) were conducted by periodically reversing the applied potential, as shown in Figures 5.7e-k. It is noted that once the GeNP was fully lithiated to \( a \)-\( \text{Li}_{15}\text{Ge}_4 \), the applied potential should be reversed immediately before \( a \)-\( \text{Li}_{15}\text{Ge}_4 \) crystallized. Such immediate potential reversal was crucial in order to further delithiate the \( a \)-\( \text{Li},\text{Ge} \) NP. In contrast, the applied potential was intentionally held for a relatively long time during the lithiation stage at the fifth cycle (Figure 5.7l), so as for \( a \)-\( \text{Li},\text{Ge} \) to crystallize to \( c \)-\( \text{Li}_{15}\text{Ge}_4 \). After crystallization, the \( c \)-\( \text{Li}_{15}\text{Ge}_4 \) phase could no longer be delithiated even with a higher reverse potential \((+2\text{V} \text{ to } +4\text{V})\). The inability of delithiation was manifested by the nearly constant volume before and after the reverse potential was applied, indicating a high affinity of \( \text{Li} \) with \( \text{Ge} \) in the \( c \)-\( \text{Li}_{15}\text{Ge}_4 \) phase.
Figure 5.7. Multi-cycling of a single $c$-GeNP. (a) The 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 -1V was applied in the lithiation process. The diameter increased to 247 nm with $a$-Li$_x$Ge formed. Then, a bias of 1V was applied to initiate delithiation. The $a$-Ge phase formed and the diameter decreased to 160 nm after full delithiation. (e-j) The second, third, and forth lithiation-delithiation cycles showing the same behavior as the first cycle, demonstrating the cyclability of the GeNP. (k, l) The fifth lithiation and crystallization. The $a$-Li$_x$Ge phase formed and then crystallized to $c$-Li$_{15}$Ge$_4$. 
To demonstrate the controlled formation of various crystalline and amorphous phases during lithiation-delithiation cycling, we conducted a separate test for a $c$-GeNP with an initial diameter of $\sim$160nm, as shown in Figure 5.8a. The pristine GeNP was single crystalline, as shown by the EDP in Figure 5.8b. A bias of -1V was applied to the $c$-GeNP with respect to Li metal electrode. After 155s, the $c$-GeNP was partially lithiated and the amorphous $a$-Li$_x$Ge phase formed (Figure 5.8c) in the lithiated shell. The corresponding EDP of $a$-Li$_x$Ge is shown in Figure 5.8d, consistent with the EDP previously observed in lithiated GeNWs.\[73\] Before $a$-Li$_x$Ge crystallized, the potential was reversed to +1V. The extraction of Li$^+$ ions from the $a$-Li$_x$Ge phase resulted in the formation of the $a$-Ge phase (Figure 5.8e), as confirmed by the EDP in Figure 5.8f. During the second cycle, $a$-GeNP was initially lithiated to $a$-Li$_x$Ge, then crystallized to $c$-Li$_{15}$Ge$_4$ (Figure 5.8g with the corresponding EDP in Figure 5.8h) under a prolonged holding of the applied voltage.
Figure 5.8. Identification of various crystalline or amorphous phases formed during lithiation-delithiation cycling. (a) A pristine GeNP. (b) EDP showing that the pristine GeNP is single crystalline. (c) A lithiated GeNP. (d) EDP showing that the amorphous lithiated phase is $\alpha$-Li$_x$Ge. (e) A fully delithiated GeNP. (f) EDP showing that the fully delithiated phase is $\alpha$-Ge. (g) A fully lithiated GeNP. (h) EDP showing that the crystalline lithiated phase is $c$-Li$_{15}$Ge$_4$.

5.4 Lithiation-delithiation results of SiNPs

The structural evolution and phase transformation of a large spherical SiNP with diameter ~ 1500 nm is shown in Figure 5.9. The typical EDP in Figure 5.3e identified it as a crystalline SiNP. A potential of -2v was applied on SiNP with respect to Li reference electrode to initiate the lithiation. After the potential is applied, the surface of the SiNP was lithiated as shown in Figure 5.9b. As the lithiation goes further (Figure 5.9c), the volume of the SiNP was expanding with the lithiation went from surface to core along the radial direction. A core-shell structure was formed with grey-contrasted shell covering dark-contrasted core. The lithiation from surface to core along the radial direction
indicated that the transportation rate of Li$^+$ ions was higher on surface than in bulk body as observed the development of core-shell structure in SiNWs. The grey-contrasted shell was amorphous Li$_x$Si phase which we will confirm the phase next. With further lithiation in Figure 5.9d, two cracks nucleated on the surface and propagated to the center of particle quickly (Figure 5.9e). In the mean time, new cracks nucleated, and propagated at different locations on the particle. Due to the cracks induced by electrochemical lithiation, the particle fractured into several small pieces at the end of lithiation. The lithiation phase transformation was confirmed by EDPs shown next in this chapter from crystalline Si to amorphous Li$_x$Si and then to crystalline Li$_{15}$Si$_4$ upon full lithiation process. This phase transformation was consistent with previous reported that of Si during lithiation.$^{[24-25, 29, 35]}$
Figure 5.9. Crack and fracture formation in a c-SiNP during lithiation. (a) A pristine c-SiNP with a diameter of ~ 1500 nm. (b-f) TEM snapshots showing the morphological evolution and volume expansion of the SiNP upon lithiation. (b) Lithiation started from the surface. (c) Lithiation-induced crystal-to-amorphous phase transformation, forming the structure with a crystalline core and an amorphous shell. (d) Cracks nucleated from the surface of nanoparticle. (e) Cracks propagated to the center of nanoparticle and new cracks appeared at other positions on the surface. (f) The lithiated nanoparticle fractured into pieces.

To further study the fracture behaviors of SiNPs, electrochemical lithiation with different size nanoparticles was conducted. Figure 5.10 shows three pristine SiNPs with diameters 500nm, 300nm, and 160nm respectively. During the lithiation in the first cycle, they all fractured and broke into pieces (Figure 5.10b, d, f) showing similar behavior to the particle which was discussed before. Even smaller SiNPs with diameters 140nm, 110nm were then examined under electrochemical lithiation. As shown in Figure 5.11, the two SiNPs were sitting next to each other on the Pt tip which ensured the two SiNPs
were under same lithiation condition. To initiate the lithiation, -2V voltage was applied to SiNPs after Li$_2$O/Li contacted with one of the SiNPs. Because of the fast Li$^+$ ions diffusion on the SiNPs surface, the lithiation of two SiNPs started nearly at the same time. Figure 5.11b shows the simultaneous volume expansions of the two SiNPs with core-shell lithiation mode. The interface between crystalline Si core and amorphous Li$_x$Si can be clearly seen due to the diffraction contrast in Figure 5.11c. It is worth noting that there existed a sharp interface in the other SiNP also. It was not clearly shown in the picture because the direction was not right to show the diffraction contrast. When the SiNPs were fully lithiated (Figure 5.11d), the crystalline Si cores were disappear. As shown by the red arrow in the picture, the bigger particle with original diameter 140nm formed one crack on one side of the particle leading fracture of this particle into two pieces. Interestingly, the smaller particle with original diameter 110nm did not crack during this lithiation process and expanded to a nearly spherical nanoparticle with diameter ~180nm, corresponding ~330% volume expansion. More SiNPs with different sizes were studied and showed a critical size about 140-160nm. SiNPs larger than the critical size were cracking and SiNPs smaller than this size were not cracking during the first lithiation process.
Figure 5.10. The fracture of SiNPs during first cycling lithiation with different diameters. (a, b) SiNP with diameter ~ 500 nm before and after lithiation. (c, d) SiNP with diameter ~ 300 nm before and after lithiation. (e, f) SiNP with diameter ~ 160 nm before and after lithiation.
Figure 5.11. The first lithiation process of two SiNPs sitting together. (a) The pristine SiNPs are 140nm, and 110nm in diameter. (b-d) The morphology evolution and phase transformation of these two SiNPs during lithiation. (d) The larger SiNP with diameter 140nm fractured after lithiation, the smaller SiNP with diameter 110nm did not fracture after lithiation.

The electrochemical lithiation-delithiation cycling behavior of SiNPs was next examined. Two small spherical SiNPs with diameters 64nm, 87nm respectively sitting next to each other were selected as shown in Figure 5.12a. A bias of -1 V was applied to SiNPs after Li₂O/Li contacting with the larger SiNP. As discussed before, these two
SiNPs started being lithiated simultaneously (Figure 5.12b) due to the fast Li\(^+\) ion diffusion on the SiNP surface even though only one of the SiNP contacted with Li\(_2\)O/Li. In Figure 5.12c, the two particles were swelling to 100nm, 134nm respectively, corresponding \(\sim 280\%\), \(\sim 260\%\) volume expansion. At this stage, the lithiation rate was slowing down and unlithiated crystalline Si cores were left covered by the lithiated amorphous Li\(_x\)Si. During this first lithiation, the sharp interface of lithiation reaction front was clearly seen in Figure 5.12b, c. Then the bias was reversed to +1V to initiate the delithiation process. The particles shrunk instantly in a uniform manner and were delithiated to the sizes of 70nm, 90nm respectively as shown in Figure 5.12d-f. The fully delithiated phase was identified as amorphous Si as examined next in this chapter. After the first cycle, repeated lithiation-delithiation was conducted by periodically reversing the applied bias. Figure 5.12g-l shows the second lithiation-delithiation cycle. Unlike in the first lithiation, sharp interface reaction front was not observed in the following lithiation processes, showing different lithiation mechanism compared with first lithiation of crystalline Si. During the whole cycling process, the two particles did not fracture even though the \(\sim 300\%\) volume expansion and fast lithiation-delithiation rate further evidencing the size dependent lithiation behavior of crystalline Si particles. It is worth noting that lithiated SiNPs with large original size could no longer be delithiated even with higher reverse potential after cracking and fracturing to pieces during the first lithiation.
Figure 5.12. Multi-cycling of two SiNPs. (a) The pristine SiNPs with a spherical shape are 87nm, and 64nm in diameter respectively. (b-c) First lithiation. The diameter increased to 134nm, and 100nm respectively with a-Li, Si formed. (d-f) First delithiation. The a-Si phase formed and the diameter decreased to 90nm and 70nm respectively after full delithiation. (g-l) The second lithiation-delithiation cycle showing the similar behavior as the first cycle, demonstrating the cyclability of the SiNPs.

Unlike GeNPs studied before, SiNPs showed strong anisotropic expansion during the first lithiation. Figure 5.13 shows three modes of anisotropic expansion due to different crystal orientation. SiNP with diameter 1500nm in Figure 5.13a was partially
lithiated to a core-shell structure as shown in Figure 5.13b. Because of the fastest lithiation rate of the \{110\} plane in crystalline Si, the inner unlithiated core exhibited a nearly squared shape with \{110\} facets and a nearly squared shape of lithiated shell profile. Another SiNP with diameter 605nm (Figure 5.13c) had a ellipse shaped lithiated shell profile (Figure 5.13d) due to different crystal orientation. Figure 5.13e, f show a small SiNP with diameter 160nm. In this partially lithiated SiNP, the unlithiated core exhibited hexagonal shape with six \{110\} faces and hexagonal shaped lithiated shell profile with six fast lithiation directions. These results were consistent with the anisotropic swelling of Si nanopillars studied by Lee et al.\cite{25} and also the modeling study by Yang et al.\cite{130}

**Figure 5.13.** Anisotropic swelling of SiNPs upon first cycle lithiation with different orientations.
To demonstrate the formation of various crystalline and amorphous phases during lithiation-delithiation cycling, we conducted a separate test for a crystalline SiNP with an initial diameter of ~150nm, as shown in Figure 5.14a. The pristine SiNP was single crystalline, as shown by the EDP in Figure 5.14b. After a bias of -1V was applied to the SiNP, the particle was partially lithiated and the amorphous $a$-Li$_x$Si phase formed (Figure 5.14c) in the lithiated shell. The corresponding EDP of $a$-Li$_x$Si is shown in Figure 5.14d. Before $a$-Li$_x$Si crystallized, the potential was reversed to +1V. The extraction of Li$^+$ ions from the $a$-Li$_x$Si phase resulted in the formation of the $a$-Si phase (Figure 5.14e), as confirmed by the EDP in Figure 5.14f. During the second cycle, $a$-SiNP was initially lithiated to $a$-Li$_x$Si, then crystallized to $c$-Li$_{15}$Si$_4$ (Figure 5.14g with the corresponding EDP in Figure 5.14h) upon full lithiation.

**Figure 5.14.** Identification of various crystalline or amorphous phases formed during lithiation-delithiation cycling of SiNP. (a) A pristine SiNP. (b) EDP showing that the pristine SiNP is single crystalline. (c) A lithiated SiNP. (d) EDP showing that the amorphous lithiated phase is $a$-Li$_x$Si with unlithiated $c$-Si core. (e) A fully delithiated SiNP. (f) EDP showing that the fully delithiated phase is $a$-Si with the unlithiated $c$-Si core. (g) A fully lithiated SiNP. (h) EDP showing that the crystalline lithiated phase is $c$-Li$_{15}$Si$_4$. 
5.5 Analysis of lithiation behaviors of GeNPs and SiNPs

The above experiments demonstrated that despite the large volume changes during electrochemical cycling, the GeNPs appeared to be unexpectedly tough, in contrast to the fragility (i.e., ease of fracture) of SiNPs. This motivated a comparative study of the lithiation behaviors of Si and Ge, which differ in several key aspects. First, the lithiation-induced swelling in c-GeNPs was nearly isotropic, in contrast to the strong anisotropic swelling in c-SiNPs and c-SiNWs. Recent studies showed that the apparent swelling behavior in c-Si and c-Ge, both of which undergo the two-phase lithiation, is critically governed by the reaction (including rate and expansion) at the two-phase boundary, i.e., the sharp interface between the crystalline core and amorphous shell. The isotropic swelling in lithiated GeNPs suggests that the Li-Ge reaction rate at the lithiation reaction front is insensitive to the crystallographic orientation of the phase boundary in GeNPs. In Figure 5.15, the typical core-shell structures in a partially lithiated SiNP (Figure 5.15a) and GeNP (Figure 5.15d) were compared. The original sizes of both NPs are around 160nm. In the SiNP, the inner unlithiated core exhibits a hexagonal shape with \{110\} facets, which arises owing to the fastest lithiation rate of the \{110\} plane in c-Si. The thickness of the lithiated shell is apparently orientation dependent, further evidencing the strong anisotropy in swelling during lithiation. In contrast, lithiation in the GeNP is nearly orientation independent, as manifested by the rounded core and the uniform thickness of the lithiated shell. The difference in the orientation dependence of lithiation in Si and Ge has a significant impact on their fracture behaviors, which will be further discussed next. Incidentally, the nearly isotropic
lithiation in Ge is consistent with the much less anisotropic wet-etching rate in Ge than in Si.\textsuperscript{[136-137]}

Figure 5.15. Lithiation-induced anisotropic swelling and fracture in a \textit{c}-SiNP \textit{versus} the isotropic swelling without fracture in a \textit{c}-GeNP. The original sizes of both Si and Ge NPs are about 160nm. (a) A partially lithiated SiNP showing the hexagon-shaped \textit{c}-Si core with the \{110\} facets. (b,c) Fracture occurred in a late stage of lithiation. The well-defined fracture sites are indicated by green circles. (d,e) A partially lithiated GeNP showing the rounded \textit{c}-Ge core. (f) Full lithiation without fracture of a GeNP. (g) Development of an intensified hoop tension near the fracture plane (indicated by the pink dashed line). When the anisotropic expansion occurs independently on each of \{110\} facets, a gap will form between the neighboring domains (black blocks) in the lithiated shell. To maintain the material coherency (by closing the gap), intensified hoop tension develops near the neighboring domains.

The most striking difference between SiNPs and GeNPs is their fracture behavior and cyclability. The \textit{in situ} TEM experiments have previously shown that the fracture of \textit{c}-SiNPs is size dependent; namely, above a threshold size of $\sim$150nm in diameter, surface cracks nucleated and propagated in \textit{c}-SiNPs upon the first lithiation. In contrast, all the GeNPs investigated in this work were tough without any visible crack-like defects
formed even during multiple lithiation-delithiation cycles. The fracture-free and electrochemically-cyclable features promise the GeNP as a robust, high-capacity anode material.

The tough behavior of the GeNPs is unexpected and ascribed to the isotropic nature of lithiation, as corroborated by our in situ TEM experiments and chemomechanical modeling. To appreciate the significance of such isotropy, it is essential to understand why the large $c$-SiNPs undergoing anisotropic swelling are fragile, but the $c$-GeNPs (with a wide size range of 100nm to submicron) undergoing isotropic swelling are not. To address this question in a clear and complete manner, it is necessary to review the key understandings of fracture in lithiated nanoparticles and nanowires that have been recently advanced by our team and other groups. Firstly, despite the compressive stress generated near the lithiation reaction front, the large lithiation-induced expansion occurring at the curved reaction front pushes out the material behind it, giving rise to a large hoop tension in the surface layer that drives the formation and propagation of surface cracks.\cite{24-25, 29, 131} Secondly, when the particle size is small enough to be comparable to the surface flaw size, the driving force of surface cracking, i.e., strain energy release rate, becomes dependent on the particle size. Such a size-scaling explains the existence of the critical particle size above which fracture occurs upon lithiation.

While both the surface cracking and the size dependence of fracture have been rationalized, the effects of isotropic versus anisotropic lithiation on fracture are not accounted for in the aforementioned fracture analyses.\cite{24-25, 29, 131} It is showed that the lithiation isotropy turns out to be critical to the tough behavior of $c$-Ge, as opposed to the fragility of $c$-Si. In this regard, a key observation from the \textit{in situ} TEM experiments of
lithiation in $c$-SiNPs is the symmetry breaking of fracture in the circumferential direction. That is, fracture usually occurs on the well-defined angular site (indicated by green circles in Figure 5.15a-c), which is located on one of the diameter planes (dashed line in Figure 5.15g) that passes through the opposite vertices of the hexagon-shaped $c$-Si core. Such well-defined fracture planes have also been reported in a recent experiment for $c$-SiNWs,$^{[25]}$ showing the fracture sites consistent with our observations. This characteristic fracture mode implies the existence of intensified hoop tension in these planes that likely originates from the anisotropic lithiation strain, as schematically illustrated in Figure 5.15g. At the respective {110} facets of the reaction front, the anisotropic lithiation strain could be dominated by the large expansion normal to the facets, resulting in a gap between the neighboring domains that are assumed to be lithiated independently. To maintain material coherency (i.e., deformation compatibility), the large hoop tension arises near the interface plane of the neighboring domains in order to close the gap.

To further appreciate the symmetry breaking of fracture in the circumferential direction as dictated by the anisotropy of lithiation strain, a recently developed continuum chemomechanical model was invoked to simulate the concurrent processes of phase transformation and stress evolution during lithiation of a $c$-Si nanowire. The use of the nanowire geometry simplifies the analysis, while capturing the essential physics. In the model, a sharp reaction front with an abrupt change of the normalized Li concentration from zero ($c$-Si) to one ($a$-$Li_{15}Si_{4}$) is prescribed to move in the $\langle 110 \rangle$ direction.$^{[130]}$ The total strain $\varepsilon_{ij}$ consists of three parts, $\varepsilon_{ij} = \varepsilon_{ij}^{c} + \varepsilon_{ij}^{e} + \varepsilon_{ij}^{p}$. That is, $\varepsilon_{ij}^{c}$ is the chemical strain given by $\varepsilon_{ij}^{c} = \beta_{ij}c$ (where $c$ denotes the local normalized Li concentration and $\beta_{ij}$
the expansion coefficient), $\varepsilon_{ij}^e$ is the elastic strain, and $\varepsilon_{ij}^p$ is the plastic strain. Here, the diagonal components of $\beta_{ij}$ are allowed to take different values in the local coordinate system where the $x_1$ axis is aligned with the $\langle 110 \rangle$ direction (normal to the reaction front) and the $x_2$ axis is along the transverse direction of $\langle 112 \rangle$. The assignment of anisotropic $\beta_{ij}$ in our continuum model physically reflects the anisotropy of the lithiation strain that occurs at the sharp reaction front of $\{110\}$ facets, and computationally mediates the anisotropy of the total strain $\varepsilon_{ij}$, as dictated by the requirement of deformation compatibility. Figure 5.16 plots the maximal principal stress (denoted by $\sigma_1$) 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 four SiNWs. It should be noted that the principal stress 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 $\sigma_1$ 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 was also observed that the concentrated stress develops at the early stage of lithiation. 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 phase 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. The predicted fracture sites from the stress concentration analysis agree with the experimental results of SiNWs and SiNPs.

![Chemomechanical modeling of the core-shell structure and stress generation in the cross section of a lithiated nanowire.](image)

**Figure 5.16.** Chemomechanical modeling of the core-shell structure and stress generation in the cross section of a lithiated nanowire, showing the effect of the anisotropy of lithiation strain. The stress contours (the maximal principal stress) in the lithiated SiNWs indicate fracture. From left to the right, the four columns represent the morphological changes and stress generation 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.
The highly anisotropic lithiation strain in \( c \)-Si is correlated with the orientation dependent lithiation rate at the reaction front. While it has been unambiguously shown that lithiation of the \{110\} facet in \( c \)-Si involves the step-by-step ledge flow on the inclined, close-packed \{111\} layers,\(^{[57]}\) it remains unclear as to what the exact local atomic arrangement of the \( Li_xSi \) product is on the Si \{110\} facet. The atomistic origin of anisotropic lithiation strain thus warrants further study in the future. At the continuum level, the lithiation strain should be generally larger in the normal direction than the tangential direction at the reaction front, owing to the constraint of the unlithiated core. However, considering the strong orientation dependence of the reaction rate in \( c \)-Si, it is conceivable that a strong anisotropy in the lithiation strain could possibly develop at the reaction front. On the other hand, given the orientation independence of the lithiation rate in \( c \)-Ge, the lithiation strain is expected to be more isotropic in \( c \)-Ge than in \( c \)-Si. As a result, the smaller anisotropy of the lithiation strain can effectively suppress the buildup of the high, non-uniform stress, giving rise to the tough response during the first lithiation of \( c \)-Ge and subsequent cycling of \( a \)-Ge as well.

### 5.6 Summary

The electrochemical lithiation-delithiation behavior of individual GeNPs was studied with \textit{in situ} transmission electron microscopy. The results confirmed that the lithiation of GeNPs involves a two-step phase transformation: \( a \)-Ge \( \rightarrow \) \( a \)-\( Li_xGe \) \( \rightarrow \) \( c \)-\( Li_{15}Ge_4 \), with a total volume expansion of \( \sim 260\% \), consistent with previous electrochemical tests. Fast multicycling of the GeNPs between the \( a \)-Ge and \( a \)-\( Li_xGe \)
phases was demonstrated, with highly reversible expansion and contraction. In particular, our experiments demonstrated that the GeNPs with a wide size range (from 100nm to submicrons) remained robust without fracture in multiple cycles, in distinct contrast to the size-dependent fracture of SiNPs upon the first lithiation. Through a comparative study with fragile SiNPs, it was found that the anisotropy of the lithiation strain causes the non-uniform stress in the hoop direction in lithiated SiNPs, leading to fracture in the well-defined planes. In the absence of such lithiation anisotropy, the c-GeNPs experience uniform hoop tension in the surface layer without the localized high stress, and therefore remain robust throughout multicycling.

The study of anisotropic lithiation strain and fracture sheds new light onto the mitigation of electrochemically-induced mechanical degradation in high-capacity electrode materials. Going beyond the crystalline Ge and Si and amorphous Ge studied herein, it can be reasoned that amorphous SiNPs or SiNWs should also remain robust upon lithiation because of their lack of crystallography-related anisotropy in the lithiation strain. Interestingly, this prediction is consistent with a recent experimental observation of cycling of amorphous SiNPs without fracture. Eliminating the anisotropy of the lithiation strain by amorphization thus presents a novel pathway to mitigate the mechanical degradation in high-capacity electrode materials. In addition, it is noted that a lithiation-delithiation cycle is completed in a few minutes in our experiments, which is much faster than the typical charging-discharging rate for conventional battery cells. Nevertheless, the effect of the cycling rate on fracture warrants systematic study in the future. Finally, it is worth to stress that while the intrinsic tough behavior of GeNPs facilitates the electrode integrity, maintaining a stable solid electrolyte interface (SEI)
during large-strain electrochemical cycling remains an outstanding challenge in the application of high-capacity anodes for Li-ion batteries.
Chapter 6

Self-healing of Ga electrode for Lithium ion battery

Irreversible chemo-mechanical degradation of high-capacity electrode materials remains a critical issue in the development of the next-generation LIBs. This chapter shows the self-healing behavior of gallium nanodroplets (GaNDs) under electrochemical cycling using in situ TEM. During lithiation, the GaNDs in the amorphous phase underwent liquid-to-solid phase transition, forming a crystalline phase (Li$_x$Ga) with ~160% volume expansion. The fully lithiated GaNDs exhibited highly distorted morphologies, owing to the uneven Li flow induced by the constraining effects to the GaND expansion during lithiation. Upon delithiation, the reverse phase transition occurred, and electrochemical extraction of Li led to the nucleation and growth of a nanovoid inside the GaNDs. After the GaNDs were fully delithiated, the nanovoid gradually annihilated, exhibiting a self-healing behavior. Our kinetics analysis shows that the void growth obeys a logarithmic time law while the annihilation follows a cubic function. We developed a phase field model with which we revealed that the nucleation and growth morphologies of the nanovoid depend critically on the normality of the Li concentration gradient to the GaND surface. The self-healing capability of GaNDs opens up a new pathway for mitigating the chemo-mechanical degradation of high-capacity electrodes.
6.1 Introduction

The demand for high-performance LIBs has led to intensive search for high-capacity materials in replacement of the carbonaceous electrodes in the current battery technology.\[3-4, 9-15, 17-20\] However, commercialization of the high-capacity electrodes, such as Si, has been hindered by their rapid, irreversible capacity decay and poor cyclability due to the Li insertion/extraction induced huge volume changes and subsequent fracture.\[17, 20, 23-25\] Nanostructured designs and composite strategies have been proposed to mitigate the capacity fading of the high-capacity electrode materials. Despite the rapid progress in the recent battery research, chemomechanical degradation of electrodes remains a serious issue for the development of next-generation LIBs. Gallium (Ga), a liquid metal at near room temperature, undergoes reversible liquid-to-solid transition during electrochemical lithiation/delithiation cycles.\[145\]. Conceiving a Ga composite electrode constituted of active components (such as Si) in which crack nucleation and growth are likely to occur during lithiation,\[24, 37\] Ga may serve as a healing agent through the flow and filling of the metallic liquid to the cracked surfaces during delithiation. Such self-healing composite electrodes may pave the way toward high-performance, failure-resistant electrodes. Despite its promising application, the electrochemical cycling behavior of Ga remains unclear.

Here, the first in situ electrochemical tests on single GaNDs using TEM was reported. These studies evidenced highly distorted morphological changes of the GaNDs during lithiation, and nanovoid nucleation, growth, and annihilation during delithiation. The kinetics analysis shows that the void follows a logarithmic growth law, but a cubic
annihilation law. We developed a phase field model\textsuperscript{[146]} to elucidate the mechanisms governing the void nucleation and growth patterns in the GaNDs during the delithiation process. The self-healing Ga electrodes offer substantial potential for the development of reliable, high-capacity composite electrodes for advanced LIBs.

### 6.2 Experimental approach

GaNDs were prepared by immersing a small piece of pure bulk Ga (99.99\% Alfa Aesar) into ethanol solution, followed by sonication for about 30 minutes at 40 °C. Since the melting point of pure Ga is \(\sim 29 \, ^\circ\text{C}\),\textsuperscript{[147]} the bulk Ga was melted into nanometer-sized droplets with diameters ranging from 100 to 600 nm after sonication. A tip-flattened Pt rod of 2mm in diameter was then immersed into the solution, and the as-prepared, dispersed GaNDs attached on the flat end of the Pt rod.

![Figure 6.1](image.png)

**Figure 6.1.** The typical TEM images of as-prepared GaNDs with spherical shape. The black part on the left is Pt rod. (a) A bigger GaND with diameter of 369 nm. (b) A smaller GaND with diameter of 166 nm.
Figure 6.1 displays two typical GaNDs with nearly perfect spherical shape due to the high surface tension. The electron diffraction pattern (EDP) discussed next in this chapter in Figure 6.6 (a) showed that the GaNDs were amorphous, denoted by $a$-Ga. To study the lithiation-delithiation cycling behavior of the GaNDs, an electrochemical device suited for \textit{in situ} TEM experiment was constructed, as schematically shown in Figure 6.2. The device consisted of three essential components: a single GaND as the working electrode attached on the Pt rod, a small piece of bulk Li metal as the counter electrode, and a naturally grown Li oxide (Li$_2$O) layer on the Li metal as the solid electrolyte. All the electrochemical tests were conducted inside a TEM operated at 300 kV with a Nanofactory TEM-scanning tunneling microscopy (STM) holder. Such \textit{in situ} TEM study enables real-time imaging of electrochemical reactions in single nanoparticles and nanowires during the lithiation-delithiation cycling.

\textbf{Figure 6.2.} Schematic illustration of the \textit{in situ} TEM experimental setup. GaNDs were attached on the edge of the Pt rod, serving as working electrode. A small piece of Li metal was scratched with a tungsten tip inside a glove box filled with Ar. Li metal was loaded into TEM with exposure time to the air less than 2 seconds. The Li metal served as reference electrode and lithium source, and the naturally-grown Li$_2$O layer on the Li metal served as the solid-state electrolyte for Li$^+$ transport. Using the piezomaneipulator (Nanofactory TEM-STM holder), the Li$_2$O/Li electrode was driven to contact the selected GaNDs. Lithiation experiments were conducted by applying a negative potential on the working electrode with respect to the counter electrode.
6.3 Lithiation of GaNDs

To initiate lithiation, a negative bias -2V was applied to the GaNDs working electrode with respect to the Li metal reference electrode. Figure 6.3 shows the morphological evolution of a GaND with a diameter of about 335nm during the first lithiation process. The GaND expanded radically in a uniform manner in the initial lithiation stage shown by Figure 6.3 (a-c). The lithiated and unlithiated regions formed a liquid core and solid shell structure, clearly distinguishable from the achromatic contrast. Similar core-shell structures have been observed in the lithiated Si and Ge nanoparticles and nanowires.\cite{24, 29, 72-73, 141-142} As lithiation proceeded, radial Li flow from the lower part of the GaND (on the side of the solid electrolyte) to the center appeared to be faster than from the upper part (on the side of the Pt substrate). The uneven inward Li flow broke the lithiation symmetry. As a result, the unlithiated core started to deviate from the circular shape. Compressive stress is expected to generate near the lithiation reaction front owing to large volume expansion.\cite{130, 148} However, the nearly incompressible unlithiated liquid core pushes out the newly produced materials behind the lithiation reaction front, generating large loop tension in the surface layer of the lithiated shell and driving the formation and propagation of surface cracks.\cite{72, 130} The cracks subsequently relax the tension in the lithiated shell, creating a pressure difference between the lithiated shell and unlithiated core. The pressure difference drives the outward flow of the liquid Ga as a way of relaxing the compressive energy of the liquid Ga core, wherein the cracks function as flow channels. The liquid Ga was fast lithiated on its way of being squeezed out, and became a solid extrusion, as shown in Figure 6.3 (f-i). The fully lithiated GaND
underwent \(~160\%\) volume expansion\[^{147}\] compared to its initial size. The EDP in Figure 6.6 (b) identified that the lithiated product is a LiGa/Li\(_2\)Ga composite in a solid crystalline phase,\[^{145, 147}\] denoted by \(c\)-Li\(_x\)Ga.

![Figure 6.3](image)

**Figure 6.3.** Phase transformation and morphological change of GaND during lithiation. (a) A pristine GaND with a diameter of \(~335\) nm. (b-i) TEM snapshots showing the distorted morphological evolution of the GaND. (b-c) The GaND was nearly uniformly lithiated, producing a lithiated shell-unlithiated core structure. (d-e) Uneven Li flow started to occur, with a faster Li flow on the bottom part than the upper part. (f-h) The liquid Ga was lithiated on its way of being squeezed out by the expanding lithiated part of the GaND, forming an extrusion at the upper-right corner. (i) Fully lithiated GaND underwent \(~160\%\) volume expansion compared to its initial size.
Another GaND with a diameter of \( \sim 370 \) nm shown in Figure 6.4 (a) had roughly the similar initial size as the previous one shown in Figure 6.3 (a), underwent different deformation mode upon lithiation. Uneven Li flow occurred at the beginning of lithiation. The side near the Li metal fast lithiated, leaving the opposite side nearly intact. This indicates that the Li diffusivity at the GaND surface is probably comparable to that in the bulk of the liquid Ga phase, in distinct contrast to other anode materials such as Si\(^{[24]}\) and Ge\(^{[72-73]}\) in which lithiation always occurs first on the surface because of much larger Li diffusivity on their surface than in the bulk. As lithiation continued, the lithiation front in the GaND gradually propagated toward the other side, giving rise to a clearly visible interface between the lithiated solid phase and unlithiated liquid phase (Figure 6.4 (d-g)). Due to the constraining effect of the Pt substrate and the solid electrolyte to the lithiation induced volume expansion, the unlithiated liquid portion of the GaND was compressed to a flattened shape. It was observed that such uneven Li flow induced irregular morphologies were common in the lithiation of GaNDs. While it remains to be explored as to the exact mechanism that triggers the uneven Li flow, the details of the geometrical constraints and of the contact condition between the GaND and the Li metal may play a critical role in the coupled lithiation-deformation process.
Figure 6.4. Phase transformation and morphological change of GaND during lithiation. (a) A pristine GaND with a diameter of ~370 nm. (b-i) TEM snapshots showing the morphological evolution of the GaND. (b-h) Lithiation started first from the lower side of the GaND, and gradually propagated to the other side, yielding a clear visible lithiation front separating the lithiation and unlithiated regions. (i) Fully lithiated and crystallized phase.
6.3 Lithiation-delithiation cycle of GaNDs

Figure 6.5 shows a lithiation-delithiation cycle of a GaND with diameter of ~168 nm. Figure 6.5 (a-c) show the lithiation process of the GaND. After lithiation, the shape of GaND was no longer spherical, due to uneven inward lithium flow from different orientations. After lithiation the \( a \)-GaND was converted to a crystalline \( (c{-}\text{Li}, \text{Ga}) \) alloy nanoparticle. Figure 6.5 (d-i) show the delithiation process of the lithiated GaND. A bias +3 V was applied to the lithiated \( c{-}\text{Li}, \text{Ga} \) nanoparticle with respect to the Li metal reference electrode for delithiation. During delithiation, the reverse phase transitions, solid-to-liquid and \( c{-}\text{Li}, \text{Ga} \) to \( a{-}\text{Ga} \), occurred, as confirmed by the EDPs (Figure 6.6 (b-c)). Interestingly, as Li started to be extracted, two nanoscale voids were nucleated at the lower right side of the lithiated GaND shown in Figure 6.5 (d). As the delithiation continued, a new nanovoid formed between the first two as we can see in Figure 6.5 (e). After 20s of delithiation, as shown in Figure 6.5 (f), two of the formed nanovoids merged into each other to become a bigger nanovoid as the nanovoids grew. With further delithiation all of the nanovoids merged to become one large nanovoid (Figure 6.5 (g)) and the size of it increased subsequently (Figure 6.5 (g)). After the GaND was fully delithiated, and returned to the fully liquid state, the grown nanovoid diffused to the surface of GaND and collapsed.

Another GaND with diameter 148 nm was studied for the lithiation-delithiation cycle (Figure 6.6). It showed similar lithiation and delithiation behavior to the last one. During delithiation process, one single nanovoid was nucleate, grew and annihilated as indicated by the red arrows in Figure 6.6 (e-i).
Figure 6.5. Morphology evolution of the GaND (168nm in diameter) during the first cycle. (a-c) Morphology change during lithiation with volume expansion and shape change. (a) The typical TEM image of a pristine GaND (168nm in diameter). (b-c) The crystallized Li$_x$Ga is formed after pristine Ga contacted with Li$_2$O/Li electrode with a -2 V bias. (d-i) Voids formation and evolution during delithiation process. (d) The void appears at the beginning of delithiation. (e-h) The diameter of the formed void increases during the delithiation as shown in the pictures. (i) The void collapses out of the surface at the end of delithiation and the volume shrinks compared to the lithiated state.
Figure 6.6. Morphology evolution of another GaND (148nm in diameter) during the first cycle. It showed the similar lithiation and delithiation behavior to the previous one.

To identify all the phases involved during lithiation-delithiation cycle, a series of EDPs have been taken shown in Figure 6.7. The lithiation phase transformation of $a$-Ga → $c$-Li$_x$Ga was identified by the EDPs in Figure 6.7 (a) and (b), consistent with the XRD diffraction results from conventional electrochemical tests. This stage of phase transformation involved liquid-state to solid-state and amorphous to crystalline state. The
Li-Ga phase diagram\textsuperscript{[147]} indicates that the pure Ga metal has a melting point is 29 °C and the Li\texttextsubscript{x}Ga alloys such as LiGa and Li\texttextsubscript{2}Ga have melting points 730 °C and 477 °C respectively. The delithiation phase transformation of \(c\)-Li\texttextsubscript{x}Ga \(\rightarrow\) \(a\)-Ga was identified by the EDPs in Figure 6.7 (b) and (c). After fully delithiation, solid crystal Li\texttextsubscript{x}Ga alloy phase transformed to liquid \(a\)-Ga covered by Li\textsubscript{2}O on the surface (Figure 6.7 (c)).

**Figure 6.7.** The typical EDPs showing the phase transformations from \(a\)-Ga phase to \(c\)-Li\texttextsubscript{x}Ga phase and back to \(a\)-Ga phase during cycling process. (a) EDP of the pristine \(a\)-GaND has 3 rings close to the BCC (Body Centered Cubic) Ga (420),(220), and(211) planes. (b) EDP of the lithiated phase shows the reaction products are FCC (Face Centered Cubic) LiGa and Orthorhombic Li\textsubscript{2}Ga. (c) EDP of the delithiated phase shows the \(a\)-Ga and the FCC Li\textsubscript{2}O which formed on the surface of \(a\)-Ga.

To further identify the fully lithiated \(c\)-Li\texttextsubscript{x}Ga phase, a high resolution image was taken after \(a\)-GaND was fully lithiated as shown by Figure 6.8. Single crystal region and poly crystal region with moiré pattern were observed. Fast Fourier transform (FFT) was performed for the single crystal region as shown in Figure 6.9 to analysis this HRTEM image. The FFT result was similar to EDP. Compared with XRD data, this single crystal phase was indexed as cubic GaLi with zone axis [110]. The same FFT analysis was processed for the poly crystal region with moiré pattern (Figure 6.10). The primary FFT pattern shown by the red circles in Figure 6.10 (b) was the same as the FFT pattern in
Figure 6.9, indicating that it had the cubic GaLi phase. Another pattern (Figure 6.10 (c)) was indexed as orthorhombic GaLi$_2$ with zone axis [1\overline{1}2]. Using the pattern shown in Figure 6.10 (b), inverse FFT (IFFT) image was obtained in Figure 6.10 (d) showing the lattice of cubic GaLi. Similarly, the orthorhombic GaLi$_2$ lattice was shown in Figure 6.10 (e) by performing IFFT for the pattern in Figure 6.10 (c). Superposition of image (d) and (e) showed the same moiré pattern with higher contrast compared to the HRTEM image. These results verified that the fully lithiated phase was poly crystalline including cubic GaLi and orthorhombic GaLi$_2$.

![HRTEM image of fully lithiated $c$-Li$_i$Ga particle.](image)

**Figure 6.8.** HRTEM image of fully lithiated $c$-Li$_i$Ga particle.
Figure 6.9. The single crystal region of fully lithiated phase and FFT analysis.

Figure 6.10. The poly crystal region of fully lithiated phase with Moiré pattern and FFT analysis. (a) HRTEM image with moiré pattern. (b) FFT of HRTEM image (a) with red circles showing the primary pattern cubic GaLi. (c) FFT of HRTEM image (a) with red circles showing another pattern orthorhombic GaLi$_2$. (d) IFFT image of primary pattern of (b) cubic GaLi. (e) IFFT image of the pattern (c) of orthorhombic GaLi$_2$. (f) Superposition of image (d) and (e).
To further determine the composition of the lithiated products, electron energy loss spectroscopy (EELS) measurements and EELS elemental mapping of Ga and Li were conducted. Figure 6.11 (a-c) shows the zero loss image of a lithiated GaND, EELS mappings of Ga and Li respectively. It is important to note that the contour of Ga map is smaller than that of the Li map because there was a thin layer of Li$_2$O on the surface of the lithiated and delithiated GaND, as identified by the EDP (Figure 6.7 (c)). The contrast in the Ga map shows the thickness distribution of the lithiated GaND. The bright area is thinner than the dark area since the electron transparency is better in thinner area. Figure 6.11 (d-f) shows the EELS spectra from a GaND before and after lithiation. The Ga plasma peak loss shifted from 13.6 eV$^{[149]}$ to 12.7 eV after lithiation (Figure 6.11 (d)) indication that the oxidation state of Ga changed during lithiation. After lithiation we observed the Li-K edge at 61.9 eV (Figure 6.11 (f)). The Ga-L edge peak underwent insignificant change during the lithiation process.
Figure 6.11. EELS spectra and maps of Ga, and Li elements of GaND after lithiation. (a) Zero loss image of the lithiated GaND. (b) EELS map of lithiated GaND shows the size of Ga is smaller than the size in the zero loss image because there exist a layer of Li$_2$O on the surface of lithiated GaND. (c) EELS map of Li of lithiated GaND. (d) Ga plasma loss peaks before and after lithiation. There is a shift from 13.6 eV to 12.7 eV during the lithiation. (e) EELS spectra of Ga-L edge before and after lithiation. (f) EELS spectra of Li-K edge after lithiation.

Figure 6.12 shows a lithiation-delithiation cycle of another GaND with diameter of ~202 nm, with a focus on the delithiation process. During lithiation, the GaND could not maintain its spherical shape (Figure 6.12(a-b)) due to the aforementioned uneven radial Li flow and constraining effects. The fully lithiated GaND consisted of a conical extrusion at the side of the solid electrolyte, resembling a water droplet dripping from a ceiling (Figure 6.12(b)). To initiate delithiation, a bias +3V was applied to the lithiated GaND with respect to the Li metal reference electrode. Due to the electrochemical Li extraction, the reverse phase transition from the solid (c-Li$_x$Ga) to liquid (a-Ga) occurred.
Interestingly, as Li started to be extracted, a nanovoid nucleated at the contact point of the GaND to the solid electrolyte (Figure 6.12 (c)). The void expanded as delithiation continued (Figure 6.12 (d-e)), reaching a maximal size when the GaND was fully delithiated (Figure 6.12 (f)). The void shape slightly deviates from a circular shape with a higher curvature at the contact point to the solid electrolyte, much like the shape of a blowing balloon. After the GaND was fully delithiated and returned to its liquid phase, we held the delithiation conditions unchanged. The nanovoid gradually shrunk and finally disappeared (Figure 6.12 (g-j)).

Figure 6.12. Void nucleation, growth, and annihilation of a GaND (~202 nm in diameter) during multiple cycling. (a) The pristine amorphous GaND in a spherical shape. (b) Lithiation induced the expansion of the GaND that deviated from the spherical shape. (c) A void nucleated at the beginning of delithiation. (d-f) The void grew during further lithiation. (f)-(j) The void gradually shrunk and finally disappeared after the GaND was fully lithiated.

Subsequent lithiation-delithiation cycles were also studied for the GaND (Figure 6.13). Similar to the first cycle shown in Figure 6.12, the distorted morphologies during lithiation, and the void nucleation, growth, and annihilation during delithiation repeated
periodically. Throughout the multiple cycling, the GaND was able to maintain its material integrity, despite void nucleation and growth and progressively increased morphological distortion. It should be noted that in Figure 6.12 (j), a crack-like defect appeared, separating the extruded area emerged at the lithiation process from the main GaND body. The crack-like defect was possibly due to the pulling force exerted by the Pt substrate and the solid electrolyte, which constrained the shrinkage of the GaND during delithiation. The crack gradually healed as the solid electrolyte moved closer to the substrate in the following lithiation-delithiation cycles.
Figure 6.13. Morphology evolution during multiple cycling process of Gallium nanodroplet. (a-c) Lithiation of the first cycle. (d-f) Delithiation of the first cycle. (g-i) Lithiation of the second cycle. (j-l) Delithiation of the second cycle. (a) The pristine amorphous Ga nanodroplet. (b) At the beginning, the diameter of the Ga nanodroplet increase and the shape is still spherical. (c) As the lithiation process going on, the volume of the Ga nanodroplet expand and the shape is not spherical any more. (d) The nucleation of the void at the beginning of the delithiation. (e-f) During the process of delithiation the void grow bigger and disappear at the end of the delithiation. (g-i) Volume expansion and crystallization of the Ga nanodroplet during the lithiation of second cycle. (j-l) Void formation and evolution during the delithiation of the second cycle.
6.4 Understanding the nanovoid formation and annihilation

To utilize Ga as a self-healing agent in failure-resistant composite electrodes, it is essential to understand the lithiation-delithiation mechanism as well as the dynamic morphological evolution during electrochemical cycling. Here, we focus on a key experimental observation on the nanovoid nucleation and growth during delithiation of $c$-Li$_x$Ga, which involve a multiscale process of local selective dealloying and long-range mass transport. Specifically, the contact point between the lithiated GaND and the solid electrolyte acts as a sink for the outward Li flux, whose strength is mediated by the applied voltage. As delithiation proceeds, the electrochemical extraction front starts from the aforementioned contact point and propagates toward the remote end of the GaND. The nanovoid co-expands with the moving front of Li extraction. The following delithiation process was thus assumed. Li atoms leave from the delithiation front and diffuse to the sink. The vacant space created by the dealloyed Li atoms merges, causing the nucleation and growth of the nanovoid. As delithiation proceeds, the distance between the void surface and the delithiation front increases. The above process repeats until the GaND is fully delithiated. It remains unknown regarding the spatial distribution of Ga and Li in the bulk phase outside the nanovoid, i.e., whether there exists a single-phase or two-phase microstructure.\[^{130, 143-144}\] In the former, a smooth and gradual change of Li concentration exists in the bulk. In the latter, the nanovoid is enclosed by a Li-poor liquid-like layer that is further surrounded by the Li-rich solid-like bulk phase with a sharp phase boundary in between. In either case, the nanovoid grows until the GaND is fully delithiated, and the resultant nanovoid is surrounded by the pure liquid phase (a-
Ga). Such delithiation mechanism through a single point sink is different from that observed in Si or Ge nanoparticles, where the entire surface effectively acts as a sink owing to the much higher Li diffusivity on the surface of Si and Ge than in the bulk.\textsuperscript{[24, 29, 72-73, 141-142]} Moreover, the development of a single major nanovoid in the delithiated GaND contrasts to the nanoporosity formation in delithiated GeNWs.\textsuperscript{[73]}

To further understand the underlying mechanisms of void nucleation and growth in GaNDs during the delithiation process, we developed a phase field model to simulate the void formation and growth dynamics.\textsuperscript{[150-151]} A complete phase-field description of the delithiation process thus requires specification of three phases: the lithiated solid Li\textsubscript{x}Ga phase (which can be a mixture of two Li-Ga compounds), a delithiated liquid Ga phase, and a void phase. Since the main purpose is to understand the shape evolution of the void, it is assumed that the bulk domain outside the nanovoid is a single Li-rich phase and the nanovoid is a Li-poor phase. A simple double-well function was employed to represent the free energy functional governing the tempo-spatial Li distribution, with the mole fraction of Li denoted as $c(x; t)$. (See details in Appendix) To mimic Li extraction, an outward Li flux $J_n$ is specified at the contact point of the solid electrolyte and the GaND, normal to the GaND surface. The gradient term in our phase field formulation plays a role of surface tension for retaining the nearly circular shape of the nanovoid. In addition, it is assumed that the Li-poor phase is perfectly non-wetting to the Li-rich phase, which corresponds to a critical boundary condition at the GaND/electrolyte contact point in order to produce the experimentally observed void shape, as detailed in Appendix. Solving the Cahn-Hilliard diffusion equation with the specified boundary conditions produces the space and time evolution of the phase field variable $c(x; t)$ and
thus the nucleation and growth morphology of the void.\textsuperscript{[152-153]} Figure 6.14 displays four snapshots of the void nucleation and growth morphologies during the delithiation of the GaND. The outward Li flux is located at the left-bottom corner of the GaND, where the void nucleates. The simulation demonstrated that the two competing processes govern the void shape: the surface rounding of the void for minimized surface energy and the Li outward flux. If the former is the relatively faster process, the void would be closer to a circular shape. Oppositely, the void would much more deviate from the circular shape. With appropriately specified parameters, the simulated void shapes resemble an inflated balloon with a necking region at the initial nucleation site, which agree qualitatively with the experimentally observed morphologies.

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{figure6.14}
\caption{Phase field modeling of void nucleation and growth during the delithiation of GaND. The green region represents the matrix phase, the white region the void phase, and the red curve the interface. The void nucleation and morphologies resemble those seen in Figure 6.13.}
\end{figure}

To understand the annihilation of the nanovoid after full delithiation, we note that the stability of the void is governed by the local chemical potential difference (\(\Delta\)) of a Ga atom on the inner and outer surfaces of the GaND. Accounting for the Gibbs-Thomson’s effect of curvature, \(\Delta\) can be written as
\[ D_m = \ln \frac{m_{\text{in}}}{m_{\text{out}}} = -2gW(1 + \frac{1}{r_{\text{in}}} + \frac{1}{r_{\text{out}}}) < 0, \]  

where \( r_{\text{in}} \) is the void radius, \( r_{\text{out}} \) the outer radius of the GaND, the surface energy of the Ga phase, and the atomic volume of Ga. Since \( < 0 \), Ga atoms tend to diffuse from the GaND surface to the void surface, leading to the shrinkage and eventual annihilation of the void. The void annihilation can be simply understood from a point of view of energy minimization. Upon annihilation of the void, the radius of the GaND shrinks to \( r_0^3 = r_{\text{out}}^3 \cdot r_{\text{in}}^3 \), based on volume conservation. The total surface area is reduced due to void annihilation, i.e., \( r_0^2 < r_{\text{out}}^2 + r_{\text{in}}^2 \), which suggests that void annihilation is driven by the reduction of the surface energy.

**Figure 6.15.** Nanovoid radius verse time (symbols) measured from in situ TEM experiment. The fitting curves (solid line) indicate that the void growth follows a logarithmic time law, while the annihilation a cubic time law.
In addition to the focused study of the physical mechanisms and energetics governing the formation and annihilation of the nanovoid, the dynamic evolution of the nanovoid size was also measured from *in situ* TEM imaging. Figure 6.15 plots the void radius as a function of time for both void growth and shrinkage, exhibiting different time laws. We found that the void growth follows a logarithmic time law of \( R = L_0 \ln(t/\tau + 1) \), with the fitting length constant \( L_0 = 26.5 \) nm and the time constant \( \tau = 1.6 \) s. The logarithmic growth has been often observed in thin film oxidation\(^{[154-155]}\) at relatively low temperatures, where oxidation proceeds by oxygen invasion through pathways of connected leakage points, in contrast to the parabolic\(^{[156]}\) growth controlled by diffusion. The logarithmic time growth could also be attributed to the leakage paths formed by connected free volumes from the delithiation front to the void phase, where the length of the leakage path increases as lithiation proceeds. Similar logarithmic time law was observed in the propagation of the nanoporous region during delithiation of Germanium nanowires GeNWs\(^{[73]}\). Figure 6.15 also shows that void annihilation follows a cubic time law: \( t \sim r_0^3 \). The void size decreases slowly at the beginning of annihilation, but sharply in the late stage. Recall that the thermodynamic driving force of void annihilation can be attributed to the curvature effect on the chemical potential of surface atoms (or equivalently of free volumes). Along the same line, the cubic time law can be derived. As shown in the Appendix, this scaling law implies that the kinetic void annihilation is rate-limited by the diffusion of the free volume in the shell between the void and the GaND surface.
6.5 Summary

The *in situ* TEM studies demonstrated dynamic morphological changes in GaNDs during electrochemical lithiation-delithiation cycling. During lithiation, the uneven Li flow, likely triggered by the geometrical constraints, leads to irregular morphologies of the fully lithiated GaNDs. During delithiation, our experiments revealed the self-healing behavior of GaNDs by showing the nucleation, growth, and annihilation of a nanovoid. The phase field modeling and theoretical analysis unraveled the void growth and annihilation mechanisms as well as the associated time laws. The reversible liquid-to-solid phase transition of Ga enables a composite design of failure-resistant electrodes consisting of Ga as the self-healing agent and other active materials such as Si.
Chapter 7

Phase Transformations of α-Fe₂O₃ Nanowires During Electrochemical Lithiation

7.1 Introduction

α-Fe₂O₃, also called hematite is the most stable iron oxide with n-type semiconducting properties under ambient conditions with rhombohedral crystal structure. Due to its advantage of being inexpensive and environmental friendliness, α-Fe₂O₃ is a potential candidate for LIB anode with a theoretical capacity of 1007mAh/g. Poizot et al.\cite{81} proposed that nanosized transition metal oxides can serve as anode material for LIBs and demonstrated their high capacity, great capacity retention, and high discharging rate. α-Fe₂O₃ nanotubes studied by Chen et al.\cite{79} and α-Fe₂O₃ nanoparticles by Larcher et al.\cite{157} have indicated that the morphology of nanometer-sized α-Fe₂O₃ structures plays a significant role, but they also observed capacity degradation occurred in all cases on long-term cycling. Lithiation and delithiation of the electrode materials in LIBs often are accompanied with large strain and structure changing in the host materials, which could cause plastic deformation and fracture. However, no in situ TEM observation data are available in the literature on nanosized α-Fe₂O₃ lithiation and delithiation. The detailed electrochemical reaction observed from in situ TEM studies during cycling may advance our understanding of the fundamental issues of nanosized transition metal oxides as anode materials in LIBs. In this chapter, in situ TEM solid and liquid cells are employed to study the lithiation behavior of α-Fe₂O₃ nanowires.
7.2 Experimental approach

The α-Fe₂O₃ nanowires are prepared by a simple Fe-H₂O reaction in the low temperature range of 350-450°C. Figures 7.1 and 7.2 show the pristine α-Fe₂O₃ nanowires used in this study. A cluster of α-Fe₂O₃ nanowires show the morphologies with diameter from ~50nm to submicrons and several microns in length. Some of the nanowires are in tapered shape. The EDP (Figure 7.1b) of this cluster of nanowires identifies the crystalline structure of α-Fe₂O₃ nanowires, consistent with the XRD data. An individual single α-Fe₂O₃ nanowire was selected as shown in Figure 7.2a with diameter of 700nm and length of 5μm. The EDP (Figure 7.2b) of this nanowire clearly shows that it is a single crystalline phase with zone axis [0001] in this view. It is worth noting that four-index Miller-Bravais notation was applied to analyze the single crystalline α-Fe₂O₃ with hexagonal structure. The HRTEM image (Figure 7.2c) also shows the crystal structure of this nanowire corresponding to the EDP in Figure 7.2b. Another tapered α-Fe₂O₃ nanowire has been analyzed in the same way (Figure 7.2d-e). It is about 3.7 μm in length and 60-160nm in diameter from one end to the other.

Figure 7.1. A cluster of α-Fe₂O₃ nanowires and the EDP indicating the nanowires are in crystalline phase.
Figure 7.2. Microstructure of individual pristine $\alpha$-$\text{Fe}_2\text{O}_3$ nanowires. (a-c) A single crystalline $\alpha$-$\text{Fe}_2\text{O}_3$ nanowire has a uniform diameter of 700nm and a length of 5 microns. EDP shows the nanowire is in single crystalline phase. HRTEM shows the surface is clean without any layer of other materials. (d-e) Another $\alpha$-$\text{Fe}_2\text{O}_3$ nanowire is tapered with diameter from 60nm to 160nm at two ends. HRTEM image shows the nanowire is covered with amorphous layer less than 1nm.
To set up the solid cell for electrochemical testing, an individual $\alpha$-Fe$_2$O$_3$ nanowire is attached to an aluminum rod with conductive epoxy, which is further attached to a piezo manipulator as shown in Figure 7.3. Li metal is attached to a tungsten with a layer of Li$_2$O formed on the surface of the Li metal as electrolyte. After loading the battery components into the TEM, the individual nanowire is manipulated \textit{in situ} and contact onto the electrolyte, completing the assembly of the nanobattery.

To set up a liquid cell nanobattery, an individual $\alpha$-Fe$_2$O$_3$ nanowire is the anode. A small piece of bulk LiCoO$_2$ is attached to an aluminum rod with conductive epoxy as the cathode. A drop of ILE is placed on the LiCoO$_2$ cathode surface as shown in Figure 7.3 as electrolyte. After loading the battery components into the TEM, the individual nanowire is manipulated in-situ and partially inserted into the electrolyte, completing the assembly of the nanobattery.

\textbf{Figure 7.3.} Schematic illustration of the \textit{in situ} nanobattery setup: individual $\alpha$-Fe$_2$O$_3$ nanowires as the working electrode, bulk Li metal as the counter electrode, and a naturally grown Li$_2$O surface layer as the solid electrolyte for solid cell setup; individual $\alpha$-Fe$_2$O$_3$ nanowires as the anode, bulk LiCoO$_2$ as cathode, and a drop of ILE as electrolyte for liquid cell setup.
7.3 Lithiation of α-Fe₂O₃ nanowires using liquid cell

First, the liquid cell nanobattery was employed to test the lithiation of α-Fe₂O₃ nanowire. In Figure 7.4a a pristine α-Fe₂O₃ nanowire is about 10 μm long and 120-320nm in diameter with tapered shape and the corresponding EDP (Figure 7.4b) indicates a crystalline structure. To initiate the lithiation which is the charging process in this experimental setup, a bias -4V was applied to the α-Fe₂O₃ nanowire with respect to the bulk LiCoO₂. It is noted that the potential over ±4V will cause the degradation of ILE and loss the capability of transporting Li⁺ ions.\(^{[53]}\) Figure 7.4c-g shows the lithiation process of this α-Fe₂O₃ nanowire. During lithiation ionic liquid migrated along the nanowire and formed droplets in the middle of the nanowire. The driving force of migrating of ionic liquid is from the applied potential and this has been studied in detail by Huang et al.\(^{[160]}\) recently. After lithiation was initiated, the α-Fe₂O₃ nanowire showed a curved shape compared to the straight shape of pristine one indicating the volume change and stress generating in nanowire. Because one layer of ILE coating on the surface of α-Fe₂O₃ nanowire was formed during lithiation and the volume expansion was small compared to that of Si, the reaction front was not clearly observed. The lithiation speed also was in a slow manner. Because of the long time lithiation, the e-beam was shut down during the experiment and only opened the e-beam for taking images. After about 3 hours lithiation, the nanowire was pulled out of the ILE (Figure 7.5). EDP was taken to identify the lithiated phase showing that the reaction products are polycrystalline body centered cubic Fe (BCC-Fe) and polycrystalline face centered cubic Li₂O (FCC-Li₂O). Figure 7.5c shows the EDP of segment of nanowire which was immersed in ILE and Figure 7.5b
shows the EDP of the segment outside IEL. They both show the texture structures of lithiated structure indicating small BCC-Fe nanoparticles formed with preferential orientation in the segment outside ILE and more random directions in immersed segment.

Figure 7.4. Morphology evolution during lithiation of $\alpha$-Fe$_2$O$_3$ nanowire using liquid cell.
Figure 7.5. Phase identification of lithiated $\alpha$-Fe$_2$O$_3$ nanowire using EDPs

7.4 Lithiation of $\alpha$-Fe$_2$O$_3$ nanowires using solid cell

To further study the lithiation of $\alpha$-Fe$_2$O$_3$ nanowire, solid cell then was used to conduct the electrochemical tests. Figure 7.6a shows the pristine $\alpha$-Fe$_2$O$_3$ nanowire with
an $\alpha$-Fe$_2$O$_3$ nanoparticle attached during the sample preparation. Because the nanowire is tapered without an uniform diameter, we use this small particle as reference position to measure the diameter change during the lithiation process. A -2V bias was applied to $\alpha$-Fe$_2$O$_3$ nanowire with respect to Li metal to overcome the potential barrier of Li$^+$ going through Li$_2$O layer to initiate the reaction. In Figure 7.6b-i red arrows marked the reaction front showing the lithiation in a fast manner compared to that in liquid cell. Seen from these low magnification images, the reaction fronts are nearly V-shaped behind which the diameter increased. According to the diameter change in the reference position from 190nm (Figure 7.6a) to 240nm (Figure 7.6i), it was about 100% volume expansion assuming the isotropic lithiation induced swelling. This volume expansion is consistent with the previous report.\footnote{159} Figure 7.6j shows that after lithiation, the nanowire was brittle.

Figure 7.6. Morphology evolution and phase transformation during lithiation of $\alpha$-Fe$_2$O$_3$ nanowire using solid cell set up.
Figure 7.7 shows the EDPs of the pristine $\alpha$-Fe$_2$O$_3$ nanowire and lithiated phase. The pristine $\alpha$-Fe$_2$O$_3$ nanowire was a single crystal and the lithiated phase was BCC-Fe with FCC-Li$_2$O. The EDP of lithiated phase has similar texture features to the one we observed in liquid cell. The texture structure EDP indicated the formation of small BCC-Fe nanoparticles after lithiation with preferential orientation.

![Figure 7.7. Phase identification of lithiated $\alpha$-Fe$_2$O$_3$ nanowire using EDPs.](image)

Another $\alpha$-Fe$_2$O$_3$ nanowire was selected to conduct electrochemical test. As shown in Figure 7.8, lithiated nanowire was curved due to the lithiation induced stress generation and deformation. It was expanded both in radial and longitudinal direction.
evidencing the isotropic lithiation induced swelling. A high magnification image shows that the reaction front is 20nm-50nm wide region rather than an atomic sharp interface. In this region, the Li\(^+\) ions were gradually inserted into α-Fe\(_2\)O\(_3\) and BCC-Fe with FCC-Li\(_2\)O phase was formed when the Li\(^+\) ions exceeded a certain amount.

Figure 7.8. Morphology evolution of α-Fe\(_2\)O\(_3\) nanowire during lithiation and high magnification image of lithiation reaction front.
7.4 HRTEM observation of Lithiation of α-Fe$_2$O$_3$ nanowires using solid cell

To further study the mechanism of lithiation of α-Fe$_2$O$_3$ nanowire, *in situ* HRTEM experiments were performed focusing on the lithiation behaviors around the reaction front in an extremely high magnification condition. First a α-Fe$_2$O$_3$ nanowire was selected as shown in Figure 7.9a tilted to a zone axis [01$ar{1}$]. Figure 7.9b and c are HRTEM images of pristine nanowire and the corresponding EDP, respectively. Figure 7.9d shows a stage of lithiation process. At this stage of lithiation, we focused the e-beam to the position of reaction front where we could observe the lithiation in detail.

Figure 7.10 is a snapshot of this *in situ* HRTEM lithiation of α-Fe$_2$O$_3$ nanowire. The lithiation proceeded from right hand side to left. In this picture, three typical regions exist. The upper-left corner is the pristine α-Fe$_2$O$_3$ region. The bottom-right corner is the fully lithiated region. In the middle is the intermediate state region. The diffusion of Li$^+$ on the surface is faster than in the bulk, so that the reaction front region is not perpendicular to the surface. It has an angle with the surface resulting V-shaped reaction front as shown in Figure 7.9d.
**Figure 7.9.** Lithiation of α-Fe₂O₃ nanowire. (a-c) The pristine α-Fe₂O₃ nanowire is single crystalline identified by EDP in (c). (d) Partially lithiated α-Fe₂O₃ nanowire.
Figure 7.10. HRTEM image of lithiation reaction front of a $\alpha$-Fe$_2$O$_3$ nanowire during lithiation showing three regions and two interface in the reaction front region.

Two typical regions are selected from Figure 7.10 to show the interfaces of the three regions. Figure 7.11a shows the interface between the pristine $\alpha$-Fe$_2$O$_3$ phase and the intermediate phase marked by the yellow dashed line. Figure 7.11b shows the interface between the intermediate phase and fully lithiated phase marked by the yellow dashed line. The two curved interfaces are very sharp with less than 1 nm width. Figure 7.11c and e are EDPs of pristine region and fully lithiated region indicating that the
pristine region is $\alpha$-Fe$_2$O$_3$ phase, and the fully lithiated region is textured BCC-Fe with FCC-Li$_2$O. To identify the phase of intermediate state, we performed a FFT analysis of the intermediate region. Figure 7.11d shows the FFT results of this region with two patterns. The red circles could be indexed as cubic Li$_x$Fe$_2$O$_3$ ($1<x<2$) with lattice constant $a=0.8422$nm. The yellow circle could be indexed as $\alpha$-Li$_x$Fe$_2$O$_3$ where $x$ is less than 1. These results are consistent with the XRD results reported by Larcher et al.$^{[157]}$

**Figure 7.11.** Phase analysis in reaction front region. (a) HRTEM image shows the pristine region and intermediate region with the interface marked by yellow dashed line. (b) The intermediate region and fully lithiation region with the interface marked by yellow dashed line. (c) The EDP of pristine region indicates that it is $\alpha$-Fe$_2$O$_3$ phase. (d) The FFT of intermediate region. We could index it with $\alpha$-Li$_x$Fe$_2$O$_3$ ($x<1$)(yellow pattern) plus cubic Li$_x$Fe$_2$O$_3$ ($1<x<2$)(red pattern). (e) The EDP of fully lithiated region indicates that it is textured BCC-Fe plus FCC-Li$_2$O.
According to the results shown in this chapter, the lithiation reaction of \( \alpha\text{-Fe}_2\text{O}_3 \) could be described as follows

\[
\alpha - \text{Fe}_2\text{O}_3 + xL_i^+ + xe^- \leftrightarrow \alpha - \text{Li}_x\text{Fe}_2\text{O}_3 \quad (0<x<1) \tag{7.1}
\]

\[
\alpha - \text{LiFe}_2\text{O}_3 + xL_i^+ + xe^- \leftrightarrow \text{Li}_x\text{Fe}_2\text{O}_3 \quad (1<x<2) \tag{7.2}
\]

\[
\text{Li}_2\text{Fe}_2\text{O}_3 + 4L_i^+ + 4e^- \leftrightarrow 2\text{Fe} + 3\text{Li}_2\text{O} \tag{7.3}
\]

At the very beginning, the \( \text{Li}^+ \) is inserted into the interstitial positions of \( \alpha\text{-Fe}_2\text{O}_3 \) without changing its rhombohedral crystal structure. After the \( \text{Li}^+ \) composition \( x \) exceeded 1, the additional \( \text{Li}^+ \) will induce a conversion of the oxygen-ion array from hexagonal to cubic close packing. This conversion could be from the shearing of the hexagonally close-packed oxygen layer to form a cubic close-packed stacking sequence.\(^{[161]}\) With more and more \( \text{Li}^+ \) inserted (when \( x \) larger than 2), the iron ions will be reduced to \( \text{Fe} \) forming BCC-Fe nanoparticles embedded in the matrix of FCC-\( \text{Li}_2\text{O} \).

### 7.5 Summary

In this chapter, by using \textit{in situ} TEM nanobatteries, the lithiation behavior of \( \alpha\text{-Fe}_2\text{O}_3 \) nanowires was studied. The high spatial resolution observation of lithiation of \( \alpha\text{-Fe}_2\text{O}_3 \) revealed the three-step lithiation process. First \( \text{Li}^+ \) ions are inserted into \( \alpha\text{-Fe}_2\text{O}_3 \), then the hexagonal structure is converted to cubic structure with more \( \text{Li}^+ \) are inserted, and the last step is the conversion reaction with formation of BCC-Fe and FCC-\( \text{Li}_2\text{O} \). These phase transformation studies are essential and important to the design of advanced electrodes with \( \alpha\text{-Fe}_2\text{O}_3 \).
Chapter 8

Conclusions and Future Work

8.1 Conclusions

In this thesis, solid cell and liquid cell nanobatteries were constructed and electrochemical test and mechanical degradation of anode materials in LIBs were conducted via in situ HRTEM. With this approach, assisted by theory and modeling, a number of nanoscale anode materials, including Si, Ge, Ga, and α-Fe₂O₃, have been studied. Different electrochemical and mechanical behaviors have been observed in situ providing valuable information for theoretical and modeling studies. These studies advanced the fundamental understanding of coupled electro-chemo-mechanical effects on the lithiation/delithiation of anode materials in LIBs. The experiments provided basic guidance for rational design of advanced LIBs. The main conclusions in the previous chapters are summarized here.

The lithiation of SiNWs using in situ TEM was studied and the morphological changes with the phase transformation from Si to Li₁₅Si₄ upon full lithiation were identified. The volume expansion of crystalline SiNWs was as large as ~300% during the first lithiation and was highly anisotropic with the predominant expansion along <110> directions and little expansion along the other directions. Accompanied with large plastic flow of the lithiation product, very large hoop stresses were generated at the outer surface of SiNPs/SiNWs, causing crack forming and fracture.
Electrochemical lithiation/delithiation behaviors of individual GeNPs and SiNPS were studied with in situ TEM. It was found that the lithiation of GeNPs involved a two-step phase transformation: \(c\text{-}\text{Ge}/a\text{-}\text{Ge} \rightarrow a\text{-}\text{Li}_x\text{Ge} \rightarrow c\text{-}\text{Li}_{15}\text{Ge}_4\), with a total volume expansion of \(~260\%\). Fast multicycling of the GeNPs between the \(a\text{-}\text{Ge}\) and \(a\text{-}\text{Li}_x\text{Ge}\) phases was demonstrated, with highly reversible expansion and contraction. The experiments demonstrated that the GeNPs with a wide size range remained robust without fracture in multiple cycles, in contrast to the size-dependent fracture of SiNPs upon the first lithiation. The lithiation of SiNPs showed similar phase transformation: \(c\text{-}\text{Si}/a\text{-}\text{Si} \rightarrow a\text{-}\text{Li}_x\text{Si} \rightarrow c\text{-}\text{Li}_{15}\text{Si}_4\). However, the expansions of SiNPs were highly anisotropic and caused the non-uniform stress in the hoop direction in lithiated SiNPs, leading to fracture in the well-defined planes. The studies of the anisotropic lithiation strain and fracture shed new light onto the mitigation of electrochemically-induced mechanical degradation in high-capacity electrode materials.

The lithiation/delithiation behavior of GaNDs was explored with in situ TEM. The experiments demonstrated that the GaNDs underwent reversible liquid-to-solid and amorphous to crystalline phase transitions during lithiation/delithiation cycles. During delithiation, in situ TEM experiments revealed the self-healing behavior of GaNDs by showing the nucleation, growth, and annihilation of a nanovoid. A phase field modeling and theoretical analysis unraveled the void growth and annihilation mechanisms as well as the associated time laws. The reversible liquid-to-solid phase transition of Ga enables a composite design of failure-resistant electrodes consisting of Ga as the self-healing agent and other active materials such as Si.
The lithiation mechanisms of $\alpha$-Fe$_2$O$_3$ nanowires were studied by using *in situ* TEM nanobatteries. The high spatial resolution observation of lithiation of $\alpha$-Fe$_2$O$_3$ revealed the three-step lithiation process. First Li$^+$ ions were inserted into $\alpha$-Fe$_2$O$_3$, then the hexagonal structure was converted to cubic structure after more Li$^+$ were inserted, and the last step was the conversion reaction with formation of BCC-Fe and FCC-Li$_2$O. Because of $\alpha$-Fe$_2$O$_3$ being a typical transition metal oxide, this study demonstrated the conversion reaction mechanism of lithiation of transition metal oxides electrode. These phase transformation studies are essential and important to the design of advanced LIB electrodes with transition metal oxides.

**8.2 Future work**

To further study the possibility of Ga as a self-healing agent for high capacity active materials such as Si, GaSi nanocomposites could be fabricated. With the *in situ* TEM, we could address some issues such as, the ability of Ga to heal the cracks and maintain the fractured Si together during electrochemical cycling.

Other transition metal oxides, sulfides, nitrides, phosphides, or fluorides similar to Fe$_2$O$_3$ could be potentially used as anode materials in next generation LIBs due to their higher capacities compared to that of graphite. *In situ* TEM could be used to test the reversibility of these anode materials and target other issues induced by lithiation and delithiation.

Cathode materials, such as layered oxides, usually show very small change in volume and structure compared to anode materials during lithiation/delithiation. *In situ*
TEM could be used to study the phase transformations of cathode materials in LIBs during electrochemical cycling.

In the current *in situ* TEM tests, the lithiation and delithiation were controlled by applying a constant voltage to the nanobatteries. It is worth developing an approach to perform the current control cycling of nanobatteries, such as galvanostatic charging/discharging, and cyclic voltmmetry. By using this technique, we could couple the conventional electrochemical tests with *in situ* observations of the high spatial microstructure evolution of electrodes in LIBs during cycling. The link between microstructure changes and electrochemical parameters could advance the fundamental understanding of the lithiation and delithiation mechanisms.
Appendix

Phase Field Modeling

I. Phase Field Modeling

Our phase-field model employs the tempo-spatial Li distribution $c(x; t)$ as the order parameter to illustrate the void nucleation and growth in GaNDs during the delithiation process. Since our main purpose is to understand the shape evolution of the void, the present model considers a two-phase transition process, i.e. the void phase (Li-poor phase) with a small $c$ and the matrix phase (Li-rich) with a large $c$ which is composed of lithiated solid and delithiated liquid (between void and solid) phases. Figure S1 gives the schematic of the present phase-field model.

![Figure S1](image)

**Figure S1.** Schematic of the phase-field model implemented through spectral smoothed boundary method.
The total free energy of the system is composed of the chemical energy and gradient energy,

$$F_{tot} = \int_V \left[ f_{chem}(c,T) + f_{gra}(\nabla c) \right] dV \quad (1)$$

Here the chemical energy is expressed with regular solution formulation,

$$f_{chem}(c,T) = N_v [\Lambda c (1 - c) + kT (c \ln c + (1 - c) \ln (1 - c))] \quad (2)$$

where $N_v$ is the number of atoms per unit volume, $\Lambda$ is the regular solution parameter, $k$ is the Boltzmann constant, $T$ is the absolute temperature. This double-well chemical energy function as shown in Figure S2 produces two stable phases. The gradient energy

$$f_{gra}(\nabla c) = \frac{\lambda}{2} (\nabla c)^2 \quad (3)$$

represents the penalty energy whenever an interface is introduced, where $\lambda$ is the gradient coefficient. The Cahn-Hilliard diffusion equation is used to depict the void growth dynamics starting from the GaND-electrolyte contact point where an outward Li flux $J_n$ is specified. The void nucleation is originated from that contact point and controlled by the heterogeneous nucleation process.$^{[152-153]}$ During the delithiation process, the void is covered by and tangential to GaND surface, much like a non-wetting phase to the GaND. Therefore, a boundary condition with $\theta(\nabla c, \mathbf{n}) = \pi$ is applied to the phase interface on the particle surface to control the void morphology. Here $\mathbf{n} = \frac{\mathbf{v}\psi}{|\mathbf{v}\psi|}$ is the unit inward normal vector locating on the GaND surface, and $\mathbf{n} \cdot \nabla c = \frac{\sqrt{2\Delta f}}{k} \cos \theta$ where $\Delta f = f_{chem}(c) - f_{chem}^{min}$ is the energy difference to the bulk chemical energy.$^{[152]}$ Any deviation
from this non-wetting boundary condition would lead to void spreading along the GaND surface as shown in Figure S3.

**Figure S2.** The variation of the normalized chemical energy to the Li distribution $c(x; t)$ at room temperature.

Spectral smoothed boundary method,\textsuperscript{[150]} which is able to solve the Cahn-Hilliard equation with the surface boundary conditions of arbitrary domain shape, is adopted in the present phase-field model. A domain parameter $\psi$, which has constant values inside or outside the GaND, but varies continuously across the diffused particle surface, is used to identify the GaND surface and apply the boundary conditions. The Cahn-Hilliard equation in the spectral smoothed boundary approach is written as,

$$
\frac{\partial c}{\partial t} = \nabla \cdot (\mathbf{M} \nabla \mu) = \frac{1}{\psi} \nabla \cdot \left[ \psi \mathbf{M} \nabla \left( \frac{\partial f_{\text{chem}}}{\partial c} - \frac{\lambda}{\psi} \nabla \cdot (\psi \nabla c) + \frac{\lambda}{\psi} \nabla \psi \cdot \nabla c \right) \right] + \frac{\psi}{\psi} J_n \quad (4)
$$
where $M$ is the Li mobility whose value in the void phase is assumed to be ten times larger than that in the matrix phase. Notice that the two boundary conditions, i.e. the Li outward flux and the void contact behavior to GaND, have been incorporated into the above kinetic equation.

![Figure S3](image_url)

**Figure S3.** Void nucleation and growth with $\theta(\nabla c, n) = \pi/2$.

The computational domain size is $128 \Delta x \times 128 \Delta y$ with domain parameter $\Psi = 0.5 + 0.5 \left( \tanh \frac{r_0 - r}{\zeta} \right)$, where $r_0 = 40$, $\zeta = 2.0$ and $r$ measures the displacement of any grid position to the GaND center point. The free energy related parameters are obtained from ref. 6, i.e. $N_v = 8.396 \times 10^{28}$ m$^{-3}$, $A = 59$ meV, $T = 300$ k. Moreover, the normalized outward Li flux and gradient coefficient are equal to 0.02 and 0.4 respectively.

**II. Time Law of Void Annihilation**

Owing to the curvature effect described in the main text, the chemical potential of an atom (a free volume) is higher (lower) on GaND surface than on the void surface, atoms (free volumes) tend to diffuse from the outer (inner) to the inner (outer) surface, thus filling (annihilating) the void. To derive the time law of void annihilation along the
same line of Tu and Gosele, one expresses the local equilibrium concentration of the free volume as a function of the mean curvature $\kappa$:

$$c(\kappa) = c_0 e^{-\Delta \mu_F(\kappa)/kT} \tag{5}$$

where $\Delta \mu_F(\kappa) = 2\gamma \kappa \Omega_F$ is the chemical potential difference of a free volume on the curved surface and a flat surface, $c_0$ is the local equilibrium concentration of free volume on a flat surface, $\gamma$ is the surface energy per unit area, and $\Omega_F$ the volume of the free volume. Since $|\Delta \mu_F(\kappa)/kT| \ll 1$ typically holds, one has $c(\kappa) \approx c_0 \left(1 - \frac{\Delta \mu_F(\kappa)}{kT}\right)$. On the void surface $\kappa = 1/r_{in}$, while on the GaND outer surface $\kappa = -1/r_{out}$ (The signs of the mean curvatures are defined such that they are consistent with those of the chemical potential energy differences). This follows that the local equilibrium concentration of free volume at the two surfaces is $c_{in} = c_0 \left(1 + \frac{\beta}{r_{in}}\right)$ and $c_{out} = c_0 \left(1 - \frac{\beta}{r_{out}}\right)$, respectively, where $\beta = 2\gamma \Omega_F/kT$.

Assuming a steady state process and with the two boundary conditions prescribed by $c_{in}$ and $c_{out}$, the concentration of free volume in the shell can be solved in a spherical coordinate system as:

$$c(r) = c_0 \beta \frac{r_{out} + r_{in}}{r_{out} - r_{in}} \frac{1}{r} - c_0 \beta \frac{2}{r_{out} - r_{in}} + c_0 \tag{6}$$

It follows that the flux of the free volume is

$$J_F = -D_F \frac{dc}{dr} = D_F c_0 \beta \frac{r_{out} + r_{in}}{r_{out} - r_{in}} \frac{1}{r^2} \tag{7}$$
where $D_F$ is the diffusivity constant of the free volume. The rate of change of $r_{in}$ is given by the geometrical relation at the inner surface:

$$\frac{dr_{in}}{dt} = (-J_F | r = r_{in}) \Omega_F$$ \hspace{1cm} (8)

Assuming $r_{in} \ll r_{out}$, one obtains an estimate of the time needed to fill the void

$$t \sim \frac{r_{in}^3}{D_F \Omega_F c_0 \beta}$$ \hspace{1cm} (9)
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