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NANYANG
TECHNOLOGICAL
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**FABRICATION AND CHARACTERIZATION OF MELT
SPUN SN-GE AND ITS APPLICATION IN LITHIUM-ION
BATTERIES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2015

**FABRICATION AND CHARACTERIZATION OF MELT
SPUN SN-GE AND ITS APPLICATION IN LITHIUM-ION
BATTERIES**

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School of Materials Science and Engineering

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2015

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The Best is Yet to Be!

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1. **S. Fan**, L.Y. Lim, M.F. Toney, H.H Hng, 2015 (In preparation)
2. **S. Fan**, L.Y. Lim, M.F. Toney, H.H Hng, 2015 Understanding the Reaction Pathway of Supersaturated Sn-Ge Alloy as Electrode Materials for Lithium Ion Batteries via Operando X-Ray Studies, 2015 (In preparation)
3. L.Y. Lim, **S. Fan**, M.F. Toney, H.H Hng, “In situ x-ray studies of crystalline Ge anodes with different conductive additives”, 2015 (In preparation)
4. **S. Fan**, L.Y. Lim, M.F. Toney, H.H Hng, Time Resolved in-operando XRD on the Capacity Fading and Irreversibility of Tin Anode for Lithium-ion Batteries, 2015 (In preparation)
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1. L.Y. Lim, **S. Fan**, H.H Hng and M.F. Toney. *Understanding Current-Induced Effects in Germanium Anodes for Lithium-Ion Batteries* in *MRS Spring Meeting 2015*. 6th - 10th April 2015. Moscone West, San Francisco, California.
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3. L.P. Tan, A. Suwardi, **S. Fan**, T. Sun, R.V. Ramanujan, and H.H. Hng. *Melt Spun $(\text{SnTe})_{1-x}(\text{SnSe})_x$ and the Observed Enhancement in Power Factor* in *MRS Fall Meeting 2012*. 25th - 30th Nov 2012. Hynes Convention Center and the Sheraton Boston Hotel, in Boston, Massachusetts.
4. **S. Fan**, X. Rui, S.S. Pramana, Y.Y. Tay, Q. Yan, and H.H. Hng. *Enhanced Lithium Storage Properties of Tin-based Anode Materials Prepared via Melt Spinning Process* in *The Energy and Materials Research Conference*. 20th - 22nd June 2012. Torremolinos, Spain.
5. **S. Fan** and H.H. Hng. *Investigating the Cooperative Enhancement of Capacities in Nanostructured SnSb/CNT Nanocomposites as Anode for Lithium Ion Batteries* in *Asia Oceania Top Universities League of Engineering* 10th - 12th October 2011. Tsinghua University, Beijing.
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8. **S. Fan**, J. Zhao, Q. Yan, J. Ma, and H.H. Hng. *Influence of nanoinclusions on thermoelectric properties of n-type Bi_2Te_3 nanocomposites*. in *29th International Conference on Thermoelectrics*. 30th May - 3rd June 2010. Shanghai, China.

Abstract

Intensive research on lithium-ion batteries (LIBs) is fueled by the needs and demands of current and emerging applications. LIBs of the future, not only have to possess high capacity, but they will also need to be lightweight and has the ability to charge/discharge within a short time. Sn-Ge prepared via melt spinning (MS) process is investigated in this work as potential anode materials. The melt spun Sn-Ge consists of a Ge-rich alloy phase and some amount of unreacted pure β -Sn phase. The Ge-rich alloy phase is the result of extended solid solubility imparted by rapid solidification, with 7 – 11 at. % Sn incorporated into the Ge lattice. The melt spun Sn-Ge samples generally outperformed pure Ge, pure Sn and physical mixture of pure Sn and Ge with reversible capacity of $\sim 1000 \text{ mAhg}^{-1}$ (1591 mAhcm^{-3}) over 80 cycles at a C-rate of 0.1C. Fast rate capability of good reversibility of close to 1000 mAhg^{-1} , at C-rates up to 0.5C and 500 mAhg^{-1} (795 mAhcm^{-3}) at high C-rate of 5C is attained. *Operando* X-ray studies show that Sn-Ge (MS) deviates from the usual reaction pathway. Lithiation of the unreacted Sn phase first occurs, followed by the liberation of Sn from the Sn-Ge alloy phase and concurrently, amorphization of Ge just before the onset of the lithiation of Ge. Since the Sn is liberated at $\sim 0.3 \text{ V}$, the liberated Sn species needs to compete with existing Li_xSn , a-Ge and Li_yGe phases for Li ions. This may results in some unlithiated or “unlithiated core-lithiated shell” species that act as “stoppers” to relieve stress/strain of the system by regulating volume expansion during lithiation and will only participate in the lithiation process of the following cycling. Upon delithiation, Li_xSn and Li_yGe dealloyed into amorphous Ge and crystalline β -Sn respectively. The Sn-Ge alloy phase is not recoverable. “Timed release capsule” model is proposed as the generalization of this novel reaction pathway.

Chapter 1 Introduction

1.1 Background

Global energy consumption trend indicate that oil and coal remain as dominant sources of fuels and electricity. In 2013, fossil fuel made up 87% of total world consumption, with the remaining 13% from low-carbon sources such as hydro, wind and solar. Despite the decline in use of coal in North America and Europe, usage in Asia has skyrocketed and now contributes to over 70% of coal consumption, with China alone contributing $\sim 50\%$.¹ With that, despite efforts in renewable energy sources, global carbon dioxide emissions continue to rise, which cause the worsening of climate change and global warming. In order for renewable energy to gain widespread adoption and for it to be competitive with oils and coals, storage and utilization of electricity generated from such intermittent sources are critical and requires efficient electrical energy storage (EES) systems, a key component of the electrical distribution grid.² Furthermore, due to rising fuel cost, electric vehicles (EVs) and hybrid electric vehicles (HEVs) are gaining popularity in the last couple of years and being considered in several countries as alternative means of transportation. Adoption rate of EVs and HEVs are especially significant in North America and Europe due to the stringent government regulations to regulate carbon emission.³

Batteries are ubiquitous and in particular, lithium-ion batteries (LIBs) are indisputably the most important and indispensable form of rechargeable batteries that we relied heavily in our daily life. Virtually all portable electronics devices rely on the reversible conversion between chemical and electrical energy of LIBs to perform. Undeniably,

the demand for next generation LIBs that can meet the various market needs will continue to grow. However, transformational changes in battery technologies are critical and necessary to enable the effective applications of LIBs in emerging market segments such as EES and EVs, to see a visible reduction in dependence on fossil fuels. Though existing LIB technologies are adequate for portable electronics devices, they will not be able to meet the demands for EVs and EES, which requires high power, large capacity, long cycle life, fast recharge (high rate capability) and lightweight.^{2, 4}

Almost 25 years since the inception of LIBs, remarkable research efforts have been devoted to the electrochemistry of LIBs and methods to bring about technological advancement by understanding various key components such as active materials for electrodes and suitable electrolytes. Among them, drastic improvement in capacities of electrode materials is one fundamentally crucial component for next generation LIBs. Graphite has been the predominant anode material since the launch of the first commercial LIB by Sony in 1991 because it is inexpensive, abundant and has good cycling stability. Graphite has theoretical gravimetric and volumetric capacities of 372 mAhg⁻¹ and 830 AhL⁻¹ respectively, but that is insufficient for emerging applications in EVs and EES.⁵

Group 14 elements, Silicon (Si), Germanium (Ge) and Tin (Sn) are among the most attractive alternative to graphite due to the larger amount of lithium that can be accommodated per formula unit, resulting in capacities that are at least 2.5 times that of graphite.^{6, 7} However, the use of elemental Si, Ge and Sn as anode materials is hampered by their poor cyclability. The structure undergoes huge volume variation (up

to 400 % change) during lithiation/delithiation process, causing pulverization of electrode and subsequently, loss of electrical contact and failure of electrode after several cycles. Significant efforts have been made to alleviate this issue. Size and morphology modifications, formation of amorphous phase and/or integrating carbon into the material are some of the most commonly explored routes.⁸⁻²⁴ Apart from structural alteration, it has been shown that the electrochemistry can also be modified by pairing the element with either an electrochemically active or inert element to enable the reaction to occur in a stepwise manner, with buffer phase(s) present during the reaction to alleviate the huge volume change.²⁵⁻²⁸ These strategies seek to accommodate strain due to drastic volume expansion and at the same time, shorten Li^+ diffusion path to enable better rate capability. As compared to size and morphology modifications of pure elemental Si, Sn and Ge, electrochemical active/active systems that consists solely of Group 14 elements are rarely reported.

1.2 Objectives

This work seeks to address the abovementioned knowledge gap. Among the group 14 elements (Si, Sn, Ge), Sn and Ge are chosen as they have much faster lithium diffusivities and higher electrical conductivities as compared to Si, which will have overall benefits toward Li storage properties of Sn-Ge systems. Sn-Ge type materials are currently prepared via complex chemical reactions and procedure, which is not cost effective. This work will explore a high throughput and industry ready process, melt spinning (MS) process to prepare the Sn-Ge binary system.

Three main objectives will be addressed through this work:

- (1) To determine the phase-structure of melt spun Sn-Ge
- (2) To investigate the Li storage properties of melt spun Sn-Ge
- (3) To understand the phase/structure transformations and establish the reaction pathways during (de)lithiation of melt spun Sn-Ge electrode

1.3 Scope

To establish and understand the phase-structure of melt spun Sn-Ge and its correlation to Li storage properties, this work covers the following aspects:

- i. Fabrication of Sn-Ge electrode materials via MS process
- ii. Phase structure characterization of the melt-spun Sn-Ge materials
- iii. Characterization and determination of Li storage properties of melt spun Sn-Ge
- iv. Establishment of reaction pathways and phase/structure transformation of melt spun Sn-Ge via *operando* synchrotron x-ray studies

1.4 Thesis Outline

This thesis begins with the research justification and grounds on which this work will be built upon. The objectives and scopes of this work are established and are directed towards gaining deeper insights into Sn-Ge as anode material for LIBs and understanding its electrochemistry (Chapter 1).

Chapter 2 reviews the current status of lithium-ion batteries. The key requirements of next generation LIBs are outlined, with a specific focus on anode materials. Various alternatives materials to graphite and their associated mechanisms are explained. Currents strategies for Group 14 elements and their alloys/mixtures as anode materials for LIBs are also reviewed.

Chapter 3 describes the fabrication process and the suite of characterization techniques for studying the phase structure; Li storage properties and electrochemistry of melt spun Sn-Ge materials.

Chapter 4 details the fabrication and characterization of the phase(s) and microstructure of melt spun Sn-Ge that are prepared by varying the starting precursors ratio of Sn:Ge. Several microscopy techniques, X-ray studies and Raman spectroscopy were adopted to study the phase and microstructure. The melt spun Sn-Ge is determined to consist of a Ge-rich Sn-Ge alloy phase and a residual pure Sn phase. The solubility limit of Sn-Ge is found to be extended to 7 – 10 at. % Sn in Ge lattice and is dependent on the amount of Sn present in the precursors.

Chapter 5 investigates the Li storage properties of melt spun Sn-Ge and provides preliminary insights into the reaction mechanism of melt spun Sn-Ge through *ex-situ* X-ray studies. Chapter 6 establishes the possible reaction pathways and phase/structure transformation of Sn-Ge via time resolved *operando* synchrotron X-ray studies. The Sn-Ge alloy is observed to liberate Sn atoms *in-situ* just before Li-Ge alloying occurs

during 1st lithiation. Since the Sn was liberated at ~ 0.3 V, the liberated Sn needs to compete with existing Li_xSn , $\alpha\text{-Ge}$ and Li_yGe phases for Li ions. As such, resulting in some unlithiated phases or “unlithiated core-lithiated shell” configuration among the species. Such species provide point electrical contacts for the efficient transport of electrons for the remaining duration of lithiation and only lithiated during subsequent lithiation. A “timed release capsule” model is proposed to explain this unique reaction pathway.

Chapter 7 concludes this work and outlines several future works based on the insights gained from this work.

Chapter 2 Literature Review

2.1 Lithium-ion Batteries

Batteries are electrochemical cells that store electrical energy in the form of chemical energy. Such reactions are thermodynamically favorable and occur spontaneously when two materials with different chemical potential are connected by a load. The material with lower chemical potential undergoes an oxidation reaction, resulting in the flow of electrons through an external circuit to the material with higher chemical potential, where a reduction reaction will take place. These two-half reactions occur concurrently and the conversion from chemical to electrical energy is driven by the electrons transfer that occurs through the external circuit. By convention, the material with lower chemical potential is called the anode, while the material with higher chemical potential is called the cathode on discharge.

Lithium-ion batteries are rechargeable batteries, i.e. the conversion between chemical and electrical energy is reversible. LIBs are first commercialized by Sony in 1991 and have since been the most versatile among the rechargeable batteries due to the specific power and energy range that it covers (Figure 1). LIBs remain the top choice for modern day portable electronics and among the prime candidates being considered for emerging applications such as EVs and EES. In commercial LIB, the predominant active electrodes materials for the cathode and anode are layered lithium metal oxide (e.g. LiCoO_2) and graphitic carbon (e.g. graphite or mesocarbon microbeads) respectively. These active materials are usually combined with binder such as polyvinylidene fluoride (PVDF) and conductive additives such as carbon black, prior

to deposition on metal foil current collector. A microporous polymeric membrane acting as separator is inserted between the electrodes. The separator prevents direct contact between the electrodes to minimize the possibility of short circuit, and at the same time allow the flow of ions across but not electrons. The electrodes are separated by an ion conducting but electrically insulating electrolyte, which can be in an aqueous, molten or solid solution form. Carbonate-based organic electrolyte with Li containing salt such as lithium hexafluorophosphate (LiPF_6) is the most commonly used form of electrolyte for LIBs.²⁹

In the fully charged state, Li is inserted (intercalated) in between the graphite layers and during discharge, Li will migrate from the anode through the electrolyte to the cathode side as Li^+ ions and get inserted into the cathode. Concurrently, electrons flow from the anode through an external circuit, creating current to power a load before entering the cathode (Figure 2). The discharge process continues until the potential difference between the cathode and the anode is too low, i.e. the cell is fully discharged. This process is reversed during charging by applying a potential, with the current flowing in the opposite direction and Li^+ ions are intercalated back into the anode from the cathode side. However, such reversibility is finite and LIB will ultimately fail. Reasons leading to the irreversibility include: (i) formation of an electrochemically inaccessible phase, (ii) loss of mechanical integrity and fracture that result from stress buildup during cycling. Such irreversibility is coupled with capacity losses during cycling and will eventually reduce the capacity to zero. Herein, to minimize confusion, the insertion of Li into the anode electrode during discharge will be known as lithiation and extraction of Li from anode during charge as delithiation throughout this thesis.

Figure 1 Ragone plot depicting the specific power and energy of various rechargeable batteries. Figure adapted from ref. 30.³⁰

Figure 2 Schematic of a typical LIB. Figure adapted from ref. 31 with permission from The Royal Society of Chemistry.³¹

2.2 Key Figure of Merits for LIBs

Energy density and power density make up the two most important figures of merit that characterized the performance of LIBs. The energy density is the amount of energy stored per unit mass or volume, while power density is the maximum practical sustained power output per unit mass or volume. Energy density is a critical parameter for most application, as it will dictate the weight and size of the battery pack. Energy density is given by the product of potential difference between the electrode and the capacity (Whkg^{-1}). On the other hand, power density will be important for fast charge/discharge applications (e.g. charging of EVs and consumer portable electronics, high power portable tools). Power density is a measure of the rate at which energy can be inserted/extracted from a cell. By convention, the rate capability of batteries is compared using “C-rate”. 1C rate is defined as the rate to charge/discharge a cell in one hour at constant current. ‘ n ’ C-rate can then be defined as the product of $n \times$ current density at 1C. The diffusion of Li^+ ions into/out of the cell is governed by Fick’s first law and can be expressed as:

$$\tau = L^2 / D \quad (1)$$

where τ is the characteristic time, L is the diffusion distance and D is the diffusion coefficient of ions. From Equation (1), high rate requires short diffusion distance and fast diffusivity. High power density thus call for high rate of energy transfer into/out of the cell, yet at the same time does not lead to a low energy density or damage to the cell.

The conversion from chemical to electrical energy in batteries is enabled by electron transfer. Li storage properties of batteries can thus be quantified by capacity, i.e. the amount of electrons transferred during the reaction. Capacity is conventionally expressed in mAhg^{-1} and is called the specific capacity, C_{specific} . The specific capacity of the electrode can be expressed as Equation (2):

$$C_{\text{specific}} = nF / M_r \quad (2)$$

where n is the number of electrons transferred per reaction, M_r is the molar mass of the electroactive component and F is the Faraday's constant. The overall specific capacity of a LIB cell, C_T (mAhg^{-1}) can be expressed as Equation (3):

$$\begin{aligned} C_T &= \frac{1}{(1/C_A) + (1/C_C) + (1/Q_M)} \\ &= \frac{C_A C_C Q_M}{C_A Q_M + C_C Q_M + C_A C_C} \end{aligned} \quad (3)$$

where C_A and C_C are the theoretical capacities of the anode and cathode respectively and $1/Q_M$ is the specific mass (gmAh^{-1}) of the other components in the cell.² Figure 3 shows the plot of overall specific capacity as a function of anode specific capacity. Cathode capacities at 140 mAhg^{-1} (which is the capacity of current commercial cathode materials) and 200 mAhg^{-1} (new cathode materials such as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, V_2O_5 , LiV_2O_5) are considered. From the plot, it clearly shows that in order to achieve an overall improvement in capacity of the cell, the specific capacity at the anode side needs to be $\sim 1000 \text{ mAhg}^{-1}$ and concurrently, high capacity at cathode side as well. From practical applications viewpoint, next generation LIBs not only have to possess higher capacities, but must also be lightweight and can be recharged in a short period of time.

Figure 3 Total cell capacity as a function of anode capacity at specific cathode capacities

Next generation LIBs face several challenges in trying to optimize both energy and power densities simultaneously, not only does the batteries need to possess superior Li storage properties but at the same time need to be lightweight. Figure 4 lists down several crucial parameters that need to be considered concurrently in the design of LIBs with both high energy and power densities.

Figure 4 Important parameters to consider when designing high energy and high power density LIBs

2.3 Current Anode Material for LIBs

Traditionally, graphite has been and remains to be the predominant anode materials for commercial LIBs since the first commercialized LIB by Sony in 1991. Carbonaceous materials remains to dominate due to its low cost, high abundance, good stability, outstanding kinetics (fast diffusion of lithium within graphite and good electrical conductivity) and small volume change ($\sim 10\%$).^{32, 33} In graphitic carbons, Li^+ ions are being intercalated in between the graphite layer in stages, resulting in a maximum configuration of LiC_6 (Equation 4).

The maximum theoretical capacity for LiC_6 is 372 mAhg^{-1} and is intrinsically limited by the reaction mechanism of graphitic materials. As described previously, the reaction mechanism is topotactic and while that ensure good reversibility, it also inevitably limits the maximum number of Li atoms that can be intercalated to one/two per formula unit as a result of limited reaction sites. This places a heavy penalty on the overall energy density achievable with the current choice of electrode materials. In order to increase the specific energy density, one can increase either the voltage or the overall cell capacity. Since graphitic carbon is the only anode material to date that has very good stability, the voltage and the extent of Li storage currently depends largely on the cathode crystal structure, stoichiometry and chemistry.

2.4 Next Generation Cathode Materials

Promising alternative cathode materials can be classified into three main categories based on their structure, i.e. I. Spinel, II. Olivine and III. Vanadium oxide based.³⁴⁻³⁹ Spinel LiMn_2O_4 and its related compounds are promising due to low cost and relative safety. Among the spinel cathode materials, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been widely studied due to similar capacity of $\sim 140 \text{ mAhg}^{-1}$ and a high reversible capacity at 4.7 V vs. Li/Li^+ . Ru-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized by a polymer assisted method, showed a capacity of 135 mAhg^{-1} at 10C rate between 3 and 5 V, with a capacity retention of 82.6% at the 500th cycle.⁴⁰ The improved performance has been attributed to improved Li^+ diffusion and enhanced electronic conductivity as a result of nanostructuring and Ru doping. The cyclability and rate capability of doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can be enhanced significantly by cationic substitutions (Co, Cr, Fe, Ga or Zn) and also through surface modification (AlPO_4 , ZnO , Al_2O_3 and Bi_2O_3).^{41, 42} However, due to the high working potential, the current standard electrolyte (LiPF_6 in ethylene carbonate/dimethyl carbonate) is incompatible.

Another class of promising alternative cathodes is LiFePO_4 , which is inexpensive, environmentally friendly and possess high thermal stability, and have recently been developed for commercial applications. LiFePO_4 crystallized in the orthorhombic olivine structure, where the P-O covalent bonding stabilized the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple, imparting very high thermal stability. However, discharge potential of 3.4 V vs. Li/Li^+ , very low electronic conductivity and slow lithium diffusion limits operation to low discharge rates. It remains attractive due to its compatibility with almost all organic electrolytes and at the same time provides a theoretical capacity of 170 mAhg^{-1} .

¹. Cornerstone work by Kang and Ceder shows that the rate capability of LiFePO₄ can be improved drastically by coating LiFePO₄ nanoparticles with a thin fast-ion coating layer due to efficient transport pathway.⁴³ The system was reported to be able to discharge in 10s and can be discharged to 397C with ~ 50 % capacity retention relative to 1C rate. In other work, Chung *et. al.* reported that the electrical conductivity of LiFePO₄ can be improved significantly by doping with supervalent cations (Mg²⁺, Al³⁺, Ti⁴⁺, Zr⁴⁺, Nb⁵⁺ and W⁶⁺) which increase the lattice conductivity.⁴⁴ Recently, ultrathin olivine-type nanosheets have been synthesized with high energy and power densities of 18 kWkg⁻¹ and 90 Whkg⁻¹, respectively at a high C-rate of 80C.⁴⁵ However, most spinel and olivine cathode materials have capacities not exceeding 200 mAhg⁻¹, which is insufficient to cause a drastic increase in overall battery capacity.

Due to the limited capacity of spinel and olivine based cathode materials, there are recent interests in one dimensional vanadium oxide (V₂O₅), due to the high capacity that it can achieve (over 300 mAhg⁻¹). Various 1D V₂O₅ in the form of nanowires, nanorods and nanobelts have been synthesized via hydrothermal reaction, vapour transport and electrospinning technique.⁴⁶⁻⁵⁰ Ban *et. al.* synthesized V₂O₅ crystallites through a combination of electrospinning and hydrothermal treatment, followed by annealing exhibit high Coulombic efficiency and high reversible capacity of 350 mAhg⁻¹.⁵¹ Mai and co-workers have also successfully prepared ultra-long V₂O₅ nanowires constructed from attached V₂O₅ nanorods via a low cost method using NH₄VO₃ as precursors.⁵² This novel structure exhibits a high capacity of 390 mAhg⁻¹, high Coulombic efficiency and good stability. However, V₂O₅ has a relatively low potential of ~ 3 V which will reduce the overall energy density of the cell.

From the brief review on cathode materials, attempts to improve the overall performance of LIBs by designing and engineering the right cathode materials are faced with a great deal of obstacles. Herein, there lies opportunities in finding and designing alternative anode materials that proceed via other forms of reaction mechanism that can augment anode capacity two or three fold that of graphitic carbons by accommodating more Li atoms per formula unit. Apart from high capacity, alternative anode materials also need to have low potential (but higher than Li, to prevent Li plating).

2.5 Alternative Anode Materials

Various alternative anode materials have been proposed and investigated and are shown in Figure 5. Among these candidate materials, Li metal is in fact a very attractive anode material due to its inherent high capacity of 3860 mAhg^{-1} and very low potential (0.01 V). Pioneering work on lithium batteries begins as early as 1912 but primary lithium batteries only became commercially available in early 1970s.⁵³ Unfortunately, studies show that lithium dendrites form upon repeated cycling at such low potential.³³ The lithium dendrite formation can puncture the separator and cause internal short circuit which can lead to serious safety problems. Furthermore, Li metal is highly unstable especially during charging, which can potentially cause a thermal runaway. The temperature will rise quickly to the melting point of Li and cause a violent reaction. Due to the abovementioned disadvantages which put safety at risk, Li metal is not recommended as potential alternative anode material for LIBs.

Figure 5 Potential cathode and anode electrode materials. Figure adapted from ref. 54. Reprinted with permission from Nature Publishing Group.⁵⁴

Apart from the classic intercalation of Li between layers of graphite, two other forms of reaction mechanisms have been identified namely conversion reaction and alloying reaction. Both types of reactions can accommodate at least two Li atoms per formula unit. In a conversion reaction which involves *3d*-transition metal oxides (MO, where M is Co Ni, Cu or Fe), the metal oxides usually exist in rock salt crystal structure, unlike the open framework in graphite which allows the direct insertion/extraction of Li from the structure. Lithiation thus involves a “conversion” mechanism that can be expressed in the following general formula equation (Equation 5), which through utilization of all possible oxidation states, can enable two or more electrons transfer per ion.⁵⁵

Apart from *3d*-transition metal oxides, sulfides, hydrides, nitrides and fluorides have also exhibit reversibility and stable capacity over 100 cycles.⁵⁶⁻⁵⁹ The good cyclability exhibited by metal oxides and fluorides has been attributed to the *in-situ* formation of

fine metallic nanoparticle domains embedded in an inert matrix (e.g., Li₂O or LiF). Purportedly, such configuration allows rapid mass transport due to the short diffusion distance. However, the underpinning mechanism such as electron transport pathway, the origin of large polarization and hysteresis remain unclear. Nevertheless, reports on transition metal oxides (MO, where M is Co, Ni, Cu or Fe) have demonstrate capacities of 700 mAhg⁻¹ with 100% capacity retention over 100 cycles and at high recharging rates.⁶⁰ Impressively, high capacity of 1480 mAhg⁻¹ at an average voltage of 0.5 V Li/Li⁺ have been demonstrated for the hydride system - MgH.⁵⁶

The last type of reaction mechanism is known as alloying reaction. Instead of Li insertion between layers of graphite or the *in-situ* formation of metallic nanoparticles domains embedded in an inert matrix, alloying reaction involves the formation of Li-M alloy phase (where M is an electrochemically active element/compound towards Li) during lithiation. Demonstrated by Dey in 1971, several elements were found to be able to alloy and dealloy with lithium metal electrochemically in an organic electrolyte at room temperature.⁶¹ Elements such as silicon (Si), germanium (Ge), tin (Sn), zinc (Zn), aluminium (Al) and antimony (Sb) can react reversibly with larger quantity of Li⁺ per formula unit (up to 4.4 Li⁺ ions per formula unit), giving significantly higher gravimetric and volumetric capacities as compared to carbon (Figure 6).^{6, 7, 54, 62-64} The alloying reaction can be represented by the following general equation (Equation 6):

Due to the larger quantity of Li⁺ that can be accommodated, such alloys exhibit specific capacities that significantly exceeded that of conventional graphite, e.g. Li_{4.4}Sn (990 mAhg⁻¹, 2000 mAhcm⁻³) and Li_{4.4}Si (4000 mAhg⁻¹, 2400 mAhcm⁻³).

Furthermore, their working potential lies close to that of graphite and lithium metal, which is beneficial in increasing the overall energy density of the cell.

Figure 6 Gravimetric and volumetric capacities of selected Li alloying elements. Reproduced by permission of The Royal Society of Chemistry. ⁶⁵

Although the much higher capacity is an appealing factor for high energy storage applications, the harbinger to large scale commercialization of lithium alloying anode materials lies in the great change in volume during the alloying and dealloying process. Figure 7 depicts the relative volume expansion experienced by the different types of reaction mechanism. Lithium has an atomic radius of 2.05 Å in its metallic state, which is comparatively greater than that of the host atoms (Sn: 1.72 Å, Si: 1.46 Å, Sb: 1.53 Å).⁶⁵ In the lithiated state, the uptake of large quantity of Li is accompanied by a huge increase in volume. This results in huge and inhomogeneous volume swing (up to 400%) during the Li alloying and dealloying process, which cause pulverization of the active material to occur over the course of several cycles. Pulverization leads to loss and deterioration of electrical contact between the active

materials and current collector, which cause capacity fading and ultimately failure of battery cell.

Figure 7 Relative structural change during lithiation for the various reaction type. Black circles: voids in the crystal structure, blue circles: metal and yellow circles. Reproduced from ref. 66 with permission from the Royal Society of Chemistry.⁶⁶

2.6 Group 14 Elements as Potential Anode Materials

As explained in the introduction section, for battery technologies to progress significantly, one has to choose a suitable electrode material for the anode, preferably one with capacity over 1000 mAhg^{-1} . Among Li alloy forming elements, Group 14 elements, Si, Ge and Sn are among the top three elements after Li metal in terms of gravimetric and volumetric capacities. Si has the highest gravimetric capacity and of the same order of magnitude as Li, but in terms of volumetric capacities, Si, Ge and Sn all possess comparable volumetric capacities. The electrical conductivity and diffusion coefficient of Li in Si, Ge, Sn and graphite are summarized in Table 1 for comparison. All the Group 14 elements have larger diffusion coefficient of Li as compared to

graphite. This means that Li can diffuse at a much faster rate in these elements as compared to graphite, i.e. better kinetics. On the other hand, apart from Sn, both Si and Ge exhibit poorer electrical conductivities as compared to graphite, which means that electrons transfer may be impaired.

Table 1 Electrical conductivity and diffusion coefficient of Li in Group 14 elements

Element	Electrical Conductivity (Sm^{-1})	Diffusion coefficient of Li (cm^2s^{-1})	Ref.
Si	1.00×10^{-3}	1×10^{-9}	67
Ge	1	2.1×10^{-7}	68
Sn	8.69×10^6	$6.0 \times 10^{-8} - 6.0 \times 10^{-8}$	7
C	1-2.5	$10^{-10} - 10^{-11}$	69, 70

Group 14 elements have been intensively investigated, with most works directed at understanding the mechanism behind the cracking of electrode. Beaulieu *et. al.* demonstrated via in-situ atomic force microscopy (AFM), showing qualitative evidences for the drastic volume expansion of the various Li-Sn phases during lithiation.⁷¹ Bessenhard *et. al.* investigated the volume expansion of Sn after the 1st lithiation cycle, its shrinkage upon delithiation and how volume change with further cycling via dilatometric studies. The findings show that drastic volume expansion was only observed during the first lithiation, but upon delithiation and further cycling only minor contraction/expansion occur.⁸ That means that the ability to alleviate volume expansion during first lithiation will be critical in enabling better cycle life. In light of the issue associated with cracking of electrode and rapid capacity fading, several strategies have been proposed to alleviate stress and accommodate volume changes. These strategies can be divided into three main categories: I. Size, structural and phase

modifications; II. Electrochemical manipulation; and III. Strategies involving a combination of I and II.

2.6.1 Size, Structural and Phase Modifications

Nanostructuring and the synthesis of low dimensional materials have been one of the main strategies that have been widely investigated in the past decade. The interest in preparing nano-sized materials are several folds. Firstly, by reducing the particle size, one will expect the volume variation experienced during lithiation and delithiation to be less severe and hence will be able to accommodate the strain induced by volume variation and better stability.^{62, 72} Secondly, due to the increase in interfacial area and contact area with electrolyte, kinetics of the reaction will improve.⁵⁹ More active sites are available for reactions, thus allowing a greater percentage of their theoretical capacity to be realized as compared to bulk phase. Also, the diffusion path of Li^+ ions is reduced, i.e. shorter time taken for Li^+ ions to move from one point to another.⁷³ Shorter diffusion pathway is critical for improving and realizing high rate performance. Nanosized Group 14 elements have been prepared via both physical and chemical methods, such as energy ball milling, hydrothermal synthesis, electrodeposition.^{10, 14, 16-18, 20, 24, 74-80} These methods have yield morphologies ranging from nanosized particles, nanowires, nanorods, thin films, patterned 3D structure, hollow, core shell structures etc. Recent work by Seo *et. al.* on carbon sheathed germanium nanowires shows a high reversible charge capacity of 963 mAhg^{-1} with a Coulombic efficiency of 91%, showing the vast potential of Ge as an anode material.²⁴ Magasinski *et. al.* used a hierarchical bottom-up assembly approach to form nanoscale Si that contains rigid and robust spheres with irregular channels to facilitate

rapid transport of Li ions into the particle core, whereas the particles' internal pores help to buffer the large volume change.⁸¹ Very high capacity of 1950 mAhg⁻¹ and stable cyclability are obtained.

On one hand, nanoparticles can improve cycle stability, but on the other side of the fence, nanoparticles tend to aggregate into larger particle due to high surface energy and large surface area. Agglomeration is a bane both during electrode fabrication as well as during cycling. During the electrode fabrication stage, it will be harder to get a homogenous blend of dispersed nanoparticles with carbon additives and binder when the particles form aggregation, leading to huge contact resistance.⁸² Furthermore, for agglomeration that occurred during cycling, it will give rise to higher possibility of secondary reactions between the electrode and electrolyte which will cause electrolyte decomposition. Also, agglomeration will lead to the recurrence of cracking of electrode which will ultimately lead to capacity fading.⁸³

Addressing the inhomogeneous volume expansion experienced in crystallite materials, amorphous phase has been shown to be more favorable for cycling ability. Amorphous phase undergoes smaller and more homogenous volume change, which helps to alleviate the loss of electrical contact of the active material.^{84, 85} As pulverization does not occur as easily in amorphous phase as compared to their bulk counterpart, cycling stability is greatly increased. Wang *et. al.* prepared amorphous hierarchical porous GeO_x and achieved very stable capacity of ~ 1250 mAhg⁻¹ over 60 cycles.⁸⁶ Yu *et. al.* demonstrated a three dimensional bicontinuous Au/amorphous Ge thin-film electrode with reversible capacity of 1200 mAhg⁻¹ and capacity retention of 90% over 100

cycles. Impressively, a capacity of 360 mAhg⁻¹ can still be attained at a C-rate of 60C.⁸⁷

Nanostructuring and amorphization are methods to control the rapid capacity fading of Li alloying type materials, but they are not a definitive solution to the problem. Wolfenstine *et. al.* has predicted and confirmed experimentally via indentation fracture toughness that the critical grain size (d_{crit}) below which microcracking does not occur as a result of Li alloying with Sn is unattainable.^{88, 89} In their model, the critical grain size for microcracking is expressed in Equation 7 as:

$$d_{crit} = 32.2\gamma(1-2\nu)^2 V_0^2 / E\Delta V^2 \quad (7)$$

where γ is the surface energy, ν is the Poisson's ratio, V_0 is the initial volume, E is the elastic modulus and ΔV is the change in volume. The critical grain size below which microcracking will not occur for Li_{4.4}Sn was predicted to be $d_{crit} \approx 0.002\text{nm}$. This critical grain size is 250 times smaller than the size of a Sn unit cell ($\approx 0.5\text{nm}$). Even if one restricts the lithiation to one Li per Sn (LiSn), the critical grain size will only increase by approximately 25 times to 0.05 nm. From their works on critical grain size, it can be concluded that microcracking cannot be prevented as it is impossible to obtain materials with fine enough grain size. It was then suggested that more practical remedies to alleviate the mechanical instability issue is to incorporate the Li-M alloy phase in a matrix that is either a ductile Li⁺ ion conducting matrix or one which will place them under compressive stress.⁹⁰

2.6.2 Electrochemistry Modifications

In the early mid-90s, Yang and co-workers pioneered the small domain concept as a general approach to improve the cycle life of lithium alloying type anode materials. In their work, they demonstrate that ductile materials such as tin can be cycled extensively, given that it exists as nanoparticles embedded in a matrix to prevent its agglomeration.²⁸ The separation of nanoparticles will prevent particle growth, which will otherwise cause the inability to sustain the stress induced and lead to the loss of point contact. As demonstrated by Yang *et. al.*, two phase metallic matrices such as SnAg and SnSb undergo lithiation in a stepwise manner.²⁸ During lithiation, the single-phase β -SnSb is transformed into Li_3Sb and multiple phases of Li_xSn ($x < 4.4$), which can then be reversed back to the original β -SnSb upon delithiation (Figure 8). The criteria are that both elements must be electrochemically active towards Li and have different chemical potential. This is widely known as the stepwise mechanism and by doing so, the more reactive phase will alloy with Li first and forms the Li-M phase which has a larger volume, while the unreacted ductile phase acts as the matrix to buffer the volume change of the more reactive phase, before taking part in the lithium alloying reaction itself. Stepwise mechanism helps to relieve stress by mutually buffering the large volume variation. Upon delithiation, SnSb structure is recovered, which is postulated to enhance the overall structural stability.

Figure 8 Reaction scheme of SnSb. Reprinted from Solid State Ionics, 90, J. Yang, M. Winter, and J.O. Besenhard, Small particle size multiphase Li-alloy anodes for lithium-ion-batteries., p. 281-287, Copyright 2014, with permission from Elsevier.²⁸

This concept was further extended to amorphous tin-based oxide ($\text{Sn}_{1.0}\text{B}_{0.56}\text{P}_{0.4}\text{Al}_{0.42}\text{O}_{3.60}$) (TCO) developed by Fuji which was the only commercialized LIB that makes use of a non-graphitic carbon electrode.⁹¹ The amorphous tin-based oxide was irreversibly reduced to Sn and Li_2O while the remaining components (network formers) remain electrochemically inert to Li during the 1st lithiation. Subsequently, only Sn participates in lithiation and form Li-Sn phases with Li, while the previously formed Li_2O and unreactive network formers act as an inert matrix to buffer the volume change. Courtney *et. al.* went on to investigate and proposed that the network formers and Li_2O formed during the first lithiation hinder the agglomeration of small Sn clusters.⁹² Hence, TCO is able to provide higher cycling stability, but at the expense of lower specific capacities as the amount of Li spent in forming the electrochemically inert phases are irreversible. Other systems that consist of active/inactive phase have also been investigated. The oxides of Group 14 elements have also been investigated as potential anode materials, with tin-based oxide being the most widely investigated.^{86, 93, 94} Generally, the cycling performance of the oxides is found to be superior in comparison to the pure elements. The presence of Li_2O

which not only acts as buffer, but also provide ionic conducting medium to facilitate Li^+ ions transport and keeping the electrochemically formed nano-sized elements dispersed. Apart from oxides, Sn has also been paired with Li inert metals, such as Fe, Ag.^{95, 96} $\text{Sn}_2\text{Fe-C}$ was prepared via mechanical alloying was demonstrated to show a much smaller first cycle irreversibility (as low as 80 mAhg^{-1}) and high first cycle reversible capacity of $\sim 700 \text{ mAhg}^{-1}$, as compared to tin oxide composites. Part of the original SnFe phase was observed to be restored during the delithiation process of Sn which gives better structural stability.⁹⁵ However, the working potential are often much higher than graphite which will greatly reduce the overall energy density.

Herein, active/active configuration is preferred over active/inactive configuration due to the larger reversible capacity that results from the reduced contribution from irreversible capacity. Furthermore, if the two active components can be selected from within Group 14 elements, it may be possible to result in the following: i) very large capacity may result if Si is used as one of the components, ii) working potential that is slightly higher than graphite so that it is safe yet not detrimental to overall energy density. Yet, these elements are rarely combined to explore the stepwise mechanism. So far, works on Group 14-type active/active systems are limited, with only a handful of reports in the literature on Si-Ge, Si-Sn and Sn-Ge.^{86, 97-105}

Micro-size materials are preferred over nano-size particle as they have higher tap density, and as a result, expected to offer higher volumetric capacity, a highly desirable attribute for EVs application.¹⁰⁶ However, as discussed previously, micro-size materials undergo large volume change during lithiation/delithiation, which

causes the disintegration of electrode upon repeated cycling that results in severe capacity fading. Moreover, micro-size materials have longer lithium ion/electron transport pathways that adversely limit the high rate capability.

One strategy is to integrate elements with the desired properties via alloying. In this context, alloying means the homogeneous mixing of the two precursory elements, with atoms of one elements replacing or occupying the interstitial sites in the lattice of the other. According to the thermodynamic of mixing, alloying will results in slightly higher working potential, which favors operation safety as compared to pure element. At the same time, relatively smaller volume expansion as compared to the single element phase.⁵⁴ Despite the advantages of group 14 elements, they are seldom explored as binary alloys with both elements from this group, with only a few attempts in the past.^{98, 99}

2.7 Sn-Ge as Potential Anode Materials

Although Si has a maximum theoretical capacity of $\sim 3850 \text{ mAhg}^{-1}$, it is apparent that preparing Sn-Ge alloy may be a more beneficial option. As a result of a lower effective mass compared to Si, lithium diffusion in Ge is reported to be 400 times faster than Si and an order of magnitude higher than Sn at room temperature.¹⁰⁷ Also, Sn and Ge have larger electronic conductivities than Si.^{7, 68} Crystalline Ge, just like Si has been shown to become amorphous after the first cycle due to electrochemically-driven solid state amorphization (ESA).^{108, 109} Several groups have prepared amorphous Si, Ge and have shown that due to the short range order that they exhibit, amorphous phase is able to improve cycling stability by (1) undergoing smaller and

homogeneous volume expansion/contraction, and (2) elimination of stress that resulted from phase transition.^{86, 110} Importantly, Si is known to readily form native oxide on its outermost layer. The subsequent lithiation of SiO₂ to Li silicate is irreversible, and implies a reduction in overall deliverable capacity as well as an increased **in** the weight of the battery cell, as then, a larger quantities of cathode material will be needed to supply sufficient Li⁺ ions and to compensate for the extensive loss of Li⁺ ions consumed in the irreversible process. On the other hand, Ge does not have a strong affinity to form native oxide and thus can improve the initial Coulombic efficiency of the system. Therefore, Ge will be more advantageous over Si in these aspects.

However, up to now there are only a few reports on new electrode materials synthesized by alloying Ge with active elements due to the difficulties in preparing such compounds via chemical/ wet chemistry methods.^{93, 99-101} Most importantly, Sn is highly immiscible in Ge (very low miscibility of < 1 at. %) due to the large difference in atomic size.¹¹¹ This makes the preparation of Sn-Ge alloy extremely difficult under equilibrium conditions. So far, Sn-Ge alloys have only been successful prepared exclusively via chemical routes using alkyl terminators and gas-phase laser photolysis reaction using tetramethyl-based precursors.⁹⁹⁻¹⁰² Often carbon is integrated into the system as studies have shown that the integration of carbonaceous materials helps in capacity retention.^{23, 112-114} The pioneering investigations on Sn-Ge as high capacity anode materials were conducted by J. Cho's group.⁹⁹⁻¹⁰¹ They showed that branched Sn₇₈Ge₂₂@carbon core-shell nanowires produced by thermal annealing of butyl-capped Sn₇₈Ge₂₂ particles at 600°C for 4 hrs gave high 1st charge capacity of 1107 mAhg⁻¹ at a C-rate of 0.3C (1C = 1100 mAhg⁻¹) and a corresponding Coulombic

efficiency of 88%. The core-shell nanowires also showed excellent capacities at higher C-rates (Figure 9a). Capacity retention of 88% and capacities of 973mAhg^{-1} are achieved at 8C, demonstrating stability of such nanoalloy particles at high-rate.⁹⁹ Sn₇₀Ge₃₀@carbon core-shell nanoparticles was also prepared using various alkyl terminators, followed by thermal annealing for 7 hrs (Figure 9b).¹⁰⁰ Butyl-capped nanoparticles were found to give the smallest irreversible capacities and better capacity retention, with a first charge capacity of 1040mAhg^{-1} . The results also indicate that the control of the thickness of carbon-shell is critical in maintaining longer cycle life. Nanocomposite consisting uniformly dispersed amorphous Ge between Sn nanoparticles formed from the thermal decomposition of a mixture of butyl-capped Ge gels and SnP_{0.94} at 400°C for 7 hrs was also demonstrated (Figure 9c).¹⁰¹ A 1st charge capacity of 1078mAhg^{-1} with capacity retention of 64% after 50 cycles was obtained.

Figure 9 (a) Branched Sn₇₈Ge₂₂@carbon core-shell nanowires and its voltage profile at various C-rates (Reprinted with permission from Nano Letters 7(9), 2638. Copyright 2007 American Chemical Society.) , (b) Aggregation of Sn₇₀Ge₃₀@carbon core-shell nanoparticles (Reprinted from Electrochimica Acta 54 (2008) 461 with the permission of Elsevier Science Ltd.) and (c) Nanocomposite of amorphous Ge coated Sn nanoparticles (Reproduced with permission from J. Electrochem. Soc., 156(4), A277 (2009). Copyright 2009, The Electrochemical Society).⁹⁹⁻¹⁰¹

These works demonstrate the potential of Sn-Ge alloys as electrode materials for high capacity and high C-rates applications. However, for practical applications, Sn-Ge alloys need to be efficiently produced on a large scale, yet preserving the unique microstructure necessary to achieve the various aims stated previously, which is not easily achieved via chemical synthesis routes. Furthermore, the kinetics and reaction mechanisms of Sn_xGe_{1-x} – typed anode materials are still not well understood. Hence, it will be of significant scientific interest to understand the fundamentals of such materials.

In order to design Sn-Ge alloy materials with high gravimetric and volumetric capacities and fast ion/electron transport, one will have to look beyond the conventional methods of synthesis, i.e. those that are performed under thermodynamic equilibrium conditions. Rapid solidification techniques such as electron beam melting and splat quenching, gas atomization and melt spinning, have been used extensively in the processing of numerous common industrial alloy systems over the last 60 years or

so.¹¹⁵⁻¹¹⁸ In particular, melt spinning (MS) is an attractive rapid solidification technique that has been used to create materials with interesting properties across categories. MS technique typically operates with cooling rate in the order of $10^1 - 10^7$ K/s. In a MS process, the precursor is first induction melted to molten liquid and then a thin layer of liquid is ejected through a slotted nozzle onto a water-cooled rotating drum and pulled over the drum surface. The quench rate is determined by the speed of the rotating drum. Upon contact with the cold surface of the rotating drum, the molten liquid rapidly cools and solidifies. MS technique was developed in the early twentieth century by Strange and Pim¹¹⁹, and was extended by Pond and Miller¹²⁰ in 1969 and later by Liebermann and Graham¹²¹, evolving into its current form. MS has been used extensively for the production of polymer fibres, metallic glasses as well as metastable and non-equilibrium phases which are otherwise impossible to prepare via other processing techniques.¹²²⁻¹²⁴ This is a cost effective and industrial friendly process that will be suitable for mass production of nanostructured materials with nano-size grains/amorphous microstructure. Since the precursors used are the elemental sources and processing take place in an inert environment, contamination and impurities can also be minimized.

MS technique is rarely used in the fabrication of electrode materials for LIBs and in the few instances, complex quaternary systems were prepared.¹²⁵⁻¹²⁷ Previously, we have studied the feasibility of using MS process to prepare nanostructured SnSb as anode materials for LIB.¹¹⁴ We have demonstrated both high capacity and high rate capability as a result of the unique microstructure form. Herein, this work leverage on the same process that we have reported previously to enable the pioneering work on the preparation of micro-size Sn-Ge alloy anode materials of varied compositions and

unique microstructures. After which, the Li storage properties of these novel Sn-Ge alloy materials will be investigated in detail as anode materials for LIBs.

Chapter 3 Materials and Methods

3.1 Overview of Methodology

Figure 10 Methodology workflow

Due to the complex nature of this work, a myriad of characterization techniques were used to study the phase, microstructure and phase transformation of Sn-Ge, in pristine form (as prepared from MS process) as well as *ex-situ* and *operando* in a half cell lithium-ion battery configuration to understand the Li storage properties of Sn-Ge. Novel $\text{Sn}_x\text{Ge}_{1-x}$ materials were first prepared via MS technique and then ground finely

and homogeneously to transform the melt spun material to similar particle size for comparison with physically blended mixture of pure elements. As they are novel materials, their phase and microstructure will first need to be characterized extensively. The techniques used are listed in Figure 10. Apart from understanding the microstructures and what the constituent phase(s) are in these Sn-Ge materials, their potential application as electrode materials for LIBs are also evaluated. Electrodes with $\text{Sn}_x\text{Ge}_{1-x}$ as active materials were assembled into half-cell configuration to elucidate the Li storage properties of $\text{Sn}_x\text{Ge}_{1-x}$. Finally, *operando* X-ray studies were carried out to gain insights and understanding on the electrochemical reaction mechanisms of $\text{Sn}_x\text{Ge}_{1-x}$ as active materials in lithium-ion batteries.

3.2 Preparation of Rapidly Solidified $\text{Sn}_x\text{Ge}_{1-x}$

Tin (10 μm , 99% trace metal basis, Aldrich) and germanium powder (-100 mesh, 99.999%, Alfa Aesar) were used as precursory materials. Sn and Ge powder were weighed in molar ratios of 7:3, 6:4, 4:6, 2:8 and 1:9 and cold pressed into pellets with diameter of 10 mm and height of ~ 30 mm. These cold pressed pellets were then used as the starting material for MS process. These melt spun samples will collectively be denoted as Sn-Ge (MS).

Rapidly solidified $\text{Sn}_x\text{Ge}_{1-x}$ were then prepared via MS process from the pressed pellets in an argon filled chamber using a single-roller melt-spinner (Edmund Bühler GmbH., Melt Spinner SC) with a 20cm diameter copper wheel (Figure 11). The pellets were loaded into a quartz tube with a 1 mm circular orifice at the nozzle and attached

onto the sample holder. The distance between the surface of the copper wheel and bottom of the nozzle was set at 0.5 mm, and rolling rate of the wheel was fixed at 60 Hz (~ 38 m/s), which is the maximum allowed rate within safety limits for this equipment and configuration. The quartz tube is positioned such that the pressed pellets lies within the radio frequency induction heating coil to ensure effective heating. The pressed pellets were induction melted to fully molten liquid state within 1 min. A pressure of 600 mbar was then introduced into the quartz tube to eject the molten liquid out of the quartz tube. Upon contact with the rapid spinning water-cooled wheel, the molten liquid rapidly solidified into very thin flakes. The as-spun $\text{Sn}_x\text{Ge}_{1-x}$ flakes were then collected and ground using the mortar grinder mill (Retsch, RM100) for 1 hr into fine homogeneous submicron size powder.

Figure 11 Schematic of a melt spinning experiment

3.3 Phase & Microstructure Characterization

3.3.1 Field Emission Scanning Electron Microscopy

Field emission scanning electron microscope (FESEM) (JEOL, JSM-7600F) was used for microstructure analysis. The FESEM is equipped with various imaging modes. In this work, secondary electron imaging and backscattered electron imaging are the two techniques used to probe the microstructure of melt spun Sn-Ge. The microstructure was examined in pristine melt spun flakes form and after they were ground to size. Secondary electron image were captured typically with an accelerating voltage of 5 kV to understand the topological and morphological aspects of melt spun Sn-Ge. Backscattered electron (BSE) images were captured with a low angle backscattered detector in gentle beam mode at 2 kV to minimize beam damage on the sample and flat cross section surface of the sample is required due to the nature of this technique.

Prior to BSE imaging, the melt spun flake needs to undergo a cross section polishing step to obtain a clean, polished cross section to make the sample suitable for BSE imaging. Polished cross sections of the melt spun flakes were obtained using an ion beam cross polisher (JEOL, CP902). The melt spun flake was cut to length of 1 cm and then mounted onto a molybdenum stub with wax. The stub was then affixed onto the sample stage and the region to be cross sectioned selected using the attached optical microscope. A shield plate was then lowered over the top of the sample to prevent excessive sample damage during polishing (Figure 12). The chamber was evacuated to vacuum and the region to be cross section was irradiated with a broad argon ion beam with an accelerating voltage of 6 kV for 30 mins.

Figure 12 Schematic of Ion beam cross section polishing

3.3.2 Electron Probe Micro Analyzer

As the Sn-Ge samples were prepared via MS techniques which will possibly result in nano size grains and varied compositions within a very small region, electron probe micro analyzer (EPMA) offer the high precision necessary to detect such small changes. A fully integrated field emission microprobe (JEOL, JXA-8530F) equipped with 5 wavelength dispersive spectrometers (WDS), energy dispersive silicon drift detector (SDD), cathodoluminescence detector and nitrogen cold trap to reduce contamination at low voltage was used in this work. Cross section polished samples used in BSE imaging were first coated with carbon before the quantitative analysis.

3.3.3 Transmission Electron Microscopy

High-resolution transmission electron microscope (HRTEM) (JEOL, JEM-2100F) with energy dispersive x-ray spectroscopy (EDS) attachment operating at 200 kV was used to collect HRTEM images and selected area electron diffraction (SAED) patterns.

A low background double tilt sample holder (Gatan) was used. Due to the nature of TEM, i.e. intensity depends on the amount of transmitted electrons through the sample, sample thickness is critical. The ground Sn-Ge materials are dispersed in ethanol, followed by drop casting the suspension onto holey carbon copper grids.

3.3.4 Laboratory Powder X-ray Diffraction

Powder X-ray diffraction (XRD) (Bruker AXS, D8 Advance) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), equipped with LYNXEYE detector was used to extract the lattice parameters, crystallite size and constituent phases in the melt spun Sn_xGe_{1-x}. The ground Sn_xGe_{1-x} samples were loaded into low background silicon sample holder and data was accumulated over 10 - 120° 2 θ with step size of 0.05 °/s.

3.3.5 Rietveld Refinement

Rietveld refinement of pristine melt spun Sn_xGe_{1-x} samples XRD patterns were performed using TOPAS software from Bruker-AXS.¹²⁸ The refinement is based on the assumptions that i) some Sn-Ge alloy are formed as a result of rapid solidification, ii) there exists some unreacted pure elemental phases due to the extremely short processing duration. The aims of the refinement are to determine qualitatively the amount of each constituent phase and extract information on lattice parameters and crystallite size of each phase. The fundamental parameters in TOPAS and corresponding X-ray form factor as calibrated for the XRD equipment were used. For each dataset, a five-coefficient Chebychev polynomial and 1/x background, zero error, unit-cell parameters, scale factors and crystallite size were refined sequentially. Data

was first refined with β -Sn, after which the refined parameters for β -Sn was locked and reiterated with diamond cubic Ge. Rietveld refinement has its limitations, though the data is able to provide clues to whether Sn-Ge alloy is formed, it is unable to determine precisely the amount of Sn in Ge and vice versa.

3.3.6 Raman Spectroscopy

While the average structure can be determined via diffraction technique, information about the local structure and bonding environment is necessary to provide evidences for the presence of an alloy. Raman spectroscopy can provide spectroscopic evidence for alloy formation by detecting the presence or absence of a Raman shift that corresponds to the Sn-Ge bond. Sn-Ge thin films were well studied via Raman scattering methods.^{129, 130} Peak shift from the characteristic peak in a Raman spectrum indicate a change in local bonding environment, whereas the presence of addition peak will give indications of the presence of secondary bonding. By correlating experimental Raman scattering data with established data, indirect inferences can be drawn. Raman spectroscopy was performed using a confocal Raman microscopy system (WITec alpha 300 SR) with visible excitation wavelength of 532 nm on pristine samples of $\text{Sn}_x\text{Ge}_{1-x}$ to elucidate the local bonding environment of Sn-Ge.

3.3.7 X-ray Absorption Spectroscopy

The formation of alloy can only be inferred indirectly via Raman spectroscopy, but it does not provide direct evidences of the presence of a Sn-Ge alloy. X-ray absorption spectroscopy (XAS) (Figure 13) investigates the local structure of melt spun Sn-Ge,

including determining the presence of Sn-Ge bonds and its structure, through the interference of wavefunction of the ejected photoelectron with the electron wavefunction backscattered from neighboring atoms of the absorbing atom. A XAS spectrum consists of two distinct regions: the X-ray absorption near edge structure (XANES), and the extended X-ray absorption fine structure (EXAFS). XANES is a region located within 30 eV of the main absorption edge, and provides information on oxidation state and hole concentration of the absorbing species. EXAFS region is located beyond 150 eV above the absorption edge, providing insights into bond distances, coordination numbers, and species of the neighbors of the absorbing atom. For this work, analysis of the EXAFS oscillations will allow the determination of the presence of Sn-Ge alloy. Typically, the EXAFS oscillations are Fourier transformed (FT) into real space, where the peaks correspond to the presence of the nearest-neighbor interactions between the absorbing atom and its neighboring atoms.

A typical EXAFS analysis involves the use of a starting model for spectrum fitting. To determine if the as-synthesized Sn-Ge (MS) is an alloy system, two reasonable starting models were employed: a pristine diamond-cubic Ge, and an “alloy mode” built upon on the diamond-cubic structure of Ge, where some Sn atoms substitute for Ge atoms in the Ge lattice. This model assumes that all the Ge precursor added in the MS process alloys with Sn atoms. A combination of the two abovementioned models were also used in the fittings, however, due to the similarities in the Ge-Ge bond lengths, the presence of pure Ge cannot be distinguished and separated from Sn-Ge (MS). Nevertheless, the EXAFS analysis shows evidence of Sn-Ge (MS) existing as an alloy system, as would be presented in subsequent sections.

The R factor and reduced chi-squared gave indication of how well a particular model describes a system. R factor measures the misfit of data while reduced chi-squared measures the goodness of fit, where the smaller the value the better the fit (needs to be > 1 for reduced chi-squared). In addition to examining the R factor and reduced chi-square values, the presence of unphysical parameters (though very rare if the starting model is correct), such as negative coordination numbers or unphysical bond lengths, are good indication to the incorrectness of the starting model.

XAS measurements were performed at Stanford Synchrotron Radiation Lightsource (SSRL), beam line (BL) 4-1, with a double crystal Si (220) monochromator on ground $\text{Sn}_x\text{Ge}_{1-x}$ powder as well as pure elemental Ge powder as reference. Harmonic rejection was achieved by detuning the second monochromator crystal to 65 % of maximum intensity. Energy calibration was monitored using metallic Ge (11103.0 eV). The XAS spectra were recorded in transmission as previously reported.^{103, 131} Spectra were background-subtracted and normalized using ATHENA software and normalized by fitting a linear function in the pre-edge region, and a three-term quadratic polynomial function to the post-edge region, which are the default functions in Athena.¹³² To obtain the EXAFS oscillations, data were Fourier transformed (FT) in the k range of $3 - 12 \text{ \AA}^{-1}$. EXAFS analysis was carried out in ARTEMIS.¹³² Coordination numbers, N , atomic distances, R and EXAFS (variance in the absorber-scatterer distance), σ^2 were determined up to the third nearest-neighbor (NN) shell. The pristine data was fitted simultaneously with multiple k weightings (1 to 3) to reduce correlations among the fitting parameters. The amplitude reduction factor S_0^2 value is 0.79 ± 0.04 , and was determined by fitting the pristine Ge powder. This value is kept constant in subsequent data fitting.

Figure 13 A Typical X-ray Absorption Spectroscopy Setup

3. 4 Fabrication of Lithium-ion Half Cell Batteries

The working electrode is prepared by mixing active material, conductive additives and binder in the ratio of 8: 1: 1. Arc-discharged single-wall carbon nanotubes (P2-SWNT, Carbon Solutions Inc.) of low functionality were used as the conductive additive. Low functionality CNTs were chosen so that it will not lead to a significant contribution towards lithium storage, yet at the same time provide the mechanical stability so that the mechanism of melt spun Sn-Ge can be probed. Polyvinylidene fluoride (PDVF) was used as the binder. The electrode slurry was prepared by dispersing the mixture in n-methyl pyrrolidone (NMP), which acts as both the dispersing agent for the CNTs as well as the solvent for PDVF. The mixture was left to stir on a magnetic stirrer at 400 rpm for 2 days to ensure homogeneous mixing of the various components. The slurries obtained were then pasted onto pre-weighed copper foils (current collector) and dried at 55 °C for 8 hrs in a vacuum oven. After drying, the electrode was weigh again to

determine the weight of the active material on the current collector. Mass loading is typically around 1.5 mg. The electrodes were assembled into CR 2032 coin-type half cells inside an argon-filled glove box with both moisture and oxygen levels less than 1 ppm. Pre-cut Li disc was used as the counter electrode and reference electrode, Celgard 2400 membrane as the separator, LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w) as the electrolyte and Sn-Ge as the working electrode. The batteries were then sealed using a crimper.

3.4.1 Lithium Storage Properties

Galvanostatic charge and discharge cycling (NEWARE multi-channel battery test system) was performed in the voltage window of 0.01 – 1.2 V vs. Li/Li⁺ at a current density that corresponds to a C-rate of 0.1C. Current density is calculated from Equation 8, in which the theoretical capacity of the system can be determined from Equation 9.

$$J = \frac{m}{1000} \times C_{Sn-Ge} \times C-rate \quad (8)$$

$$C_{Sn-Ge} = [wt.\% Sn \times C_{Sn}] + [wt.\% Ge \times C_{Ge}] \quad (9)$$

where J is the current density, m is the mass of active materials in mg, C_{Sn-Ge} is the theoretical capacity of Sn-Ge, $C-rate$ is the current needed to discharge a cell in x hours, C_{Sn} is the maximum theoretical capacity of Sn (990 mAhg⁻¹) and C_{Ge} is the maximum theoretical capacity of Ge (1600 mAhg⁻¹).

To evaluate the high rate performance of the half cells, multi-rate cycling measurements were carried out at C-rate of 0.1C, 0.2C, 0.5C, 1C, 2C and 5C, at 10

cycles per C-rate. Cyclic voltammetry (CV) was performed with an electrochemical workstation (CHI 660C) at scan rates in the range of 0.2 – 0.5 mV/s in the potential range of 0.05 – 3.0 V. All electrochemical measurements were conducted at room temperature.

3.4.2 Volumetric Capacity

Galvanostatic electrochemical measurements represent capacity in mAhg⁻¹, which gives an indication of the weight of the battery, whereas knowing the volumetric capacity, i.e. related to the size of the battery is also important. Although in the literature, tapped density of active material is often used in the calculation of volumetric capacity, electrode (pressed) density will be used in this instance, since in practical applications, we will have to consider the electrode as a whole. The pressed thickness (t) is measured by FESEM, and average diameter (d) of electrode (1.3 cm) measured using a Vernier caliper from which the electrode density (ρ_E) can be calculated using the formula, $m/\pi d^2/4 \times t$, where m is the weight of the electrode. Volumetric capacity can then be derived via Equation 10:

$$C_{vol} = C_{wt} \times \rho_E \quad (10)$$

where C_{vol} is the volumetric capacity (mAhcm⁻³), C_{wt} is the gravimetric capacity (mAhg⁻¹) and ρ_E is the electrode density (g.cm⁻³).

3.5 *Ex-situ* Characterization of Electrode at Cut-off Voltages

Apart from determining the Li storage properties, it is also of interest to understand the phase formation/transformation that have taken place during lithiation and delithiation. The half cells were charged/discharged to various cut-off voltages and then disassembled for characterization. For *ex-situ* microstructure and phase analysis of cycled electrodes, the cells were disassembled immediately in a glovebox with moisture and oxygen content of < 0.1 ppm. The electrodes were removed from the half cell and rinsed repeatedly with dimethyl carbonate (DMC) to remove any residual electrolytes on the electrodes. The electrodes were then left to dry at room temperature inside the glovebox for approximately 24 hr prior to characterization.

Ge K edge X-ray absorption spectroscopy (XAS) measurements were performed at SSRL beamline 4-1 in fluorescence mode using multi-element Ge detector for the Sn-Ge (MS) samples at different cut-off voltages. The fluorescence measurement mode was employed as there were pinholes in the *ex situ* samples which made measurements unsuitable in transmission mode. 5-10 scans were taken per sample to reduce signal-to-noise ratio. Spectra were then background-subtracted and normalized using ATHENA software to obtain the extended x-ray absorption fine structure (EXAFS) oscillations.¹³² Data were Fourier transformed (FT) in the k range of 3 – 15 Å⁻¹. EXAFS analysis was carried out in the program ARTEMIS.¹³² For the delithiated Sn-Ge (MS) samples, only the first NN (nearest neighbour) shell was analyzed as the second and third NN contributions were smeared out due to amorphization. Coordination numbers, N, were refined for the pristine and lithiated/delithiated alloy. Individual atomic distances R and EXAFS Debye-Waller factors σ^2 were determined

for each NN shell. Each data set was fitted simultaneously with multiple k weightings (1 to 3) to reduce correlations among the fitting parameters. The amplitude reduction factor S_0^2 value is 0.82 ± 0.04 and was determined by fitting the starting elemental Ge precursor used in the MS process. This value is kept constant in the fittings of delithiated Sn-Ge (MS) samples.

3.6 *Operando* X-ray Studies

Laboratory-based *ex-situ* XRD has previously been performed on cells brought to a particular state of charge, allowed to relax and then disassembled for *ex-situ* measurements. However, changes to the electrode may have occurred during disassembly and may not provide a true picture to the chemistry of the cell. On the other hand, time-resolved *operando* characterization allows real time data collection and tracks the electrochemical reactions as they proceed. Hence, eliminating the possibility of contamination by artefacts introduced during disassembly. Also, *operando* characterization will allow the detection of transient/metastable phases that may form during the reaction which are otherwise undetectable with *ex-situ* techniques. Furthermore, the highly collimated beam of high brilliance and tunable energy of synchrotron X-ray helps to improve the quality of the data collected.

3.6.1 Time Resolved *Operando* Synchrotron X-ray Diffraction

Time resolved *operando* X-ray diffraction studies were performed at SSRL X-ray diffraction beam lines (BL 1-5, 11-3) with a photon wavelength of $0.826(5)$ Å. For

synchrotron X-ray studies of $\text{Sn}_x\text{Ge}_{1-x}$ materials, the battery half-cell needs to be assembled in a modified configuration to allow X-ray penetration through the whole cell. A transparent pouch cell configuration as shown in Figure 14 was used in all *operando* synchrotron X-ray studies. The assembly of the pouch cell was carried out in an Ar filled glovebox with both moisture and oxygen concentration < 1 ppm. The electrode was prepared the same manner as described previously in Section 3.4, Li metal ribbon as the counter electrode, and Celgard 2400 membrane soaked in electrolyte as the separator. The electrolyte consists of 1M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). Pre-taped nickel tabs (MTI Corporations) were used as current collectors to ensure effective sealing. These components were assembled in sequence as shown in Figure 13 in thick transparent polyester pouch and sides of the pouch sealed. Galvanostatic charge/discharge cycles were performed in the voltage window of 0.01 – 1.2 V vs. Li/Li^+ at a current density that corresponds to 0.1C on either MTI 8-channel battery analyzer or Biologic SP-50 potentiostat/galvanostat.

Measurements were performed in transmission mode on the assembled pouch cell (Figure 15) with an exposure time that range from 10 – 200 sec, in 5 sec to 2 min intervals. Data collection was performed simultaneously as the battery was being cycled. The detector was positioned 150 mm from the sample center. The scattering intensity was detected by a 2D image plate (MAR-345) with a pixel size of 150 μm (2300 $\times$ 2300 pixels). Data was internally calibrated using the copper diffraction peaks and processed using the Area Diffraction Machine software package.¹³³ Rietveld

refinements were performed to extract the crystallite size of Ge and Sn using TOPAS.¹²⁸

Figure 14 Exploded view of pouch cell configuration

Figure 15 X-ray Diffraction Experimental setup for *operando* study of Li-ion batteries

3.6.2 Time Resolved *Operando* X-ray Absorption Spectroscopy

As with laboratory XRD, synchrotron XRD can only probe and identify crystalline phases. However, from the literature, it has been suggested that during the alloying of Li with Ge, only $\text{Li}_{15}\text{Ge}_4$ exists in crystalline form, whereas the other Li-Ge phases are amorphous.¹³¹ Furthermore, upon delithiation and further cycling, Ge remains in amorphous state due to ESA that occurred during the first lithiation cycle. Therefore, EXAFS analysis of *operando* XAS datasets will help to provide more comprehensive insights into the phase formation and transformation, due to its ability in probing local structure of materials regardless of crystallinity. Time resolved *operando* XAS study will be especially useful in complementing time resolved *operando* XRD technique, so that both crystalline and amorphous species that form during battery cycling can be accounted for.

Operando XAS measurements were performed at SSRL beam line (BL) 4-1. The experimental configuration is the same as those described previously in section 3.3.7. Galvanostatic charge/discharge cycles were performed in the same voltage window as *operando* XRD on either MTI 8-channel battery analyzer or Biologic SP-50 potentiostat/galvanostat. Data collection was performed simultaneously in transmission mode, at 15 minutes interval as the pouch cell was being cycled.

A few reasonable starting models were fitted with each data before determining the best model for each data. The models employed include the “alloy model”, pristine Ge diamond cubic model, the “alloy model” with Ge-Li scattering path, and pristine Ge diamond cubic model with Ge-Li scattering path. Examining the R factor, reduced chi-squared values and presence of unphysical parameters helps to determine the right

model for each data. Since the various Li-Ge alloys have distinct Ge-Ge bond distances,¹³¹ examining the Ge-Ge bond distances will elucidate the identity of the amorphous Li-Ge alloys that are present during electrochemical cycling. By mapping out the local structural changes from one data to the next, and correlating to *operando* diffraction data and electrochemical data, the reaction mechanism and phase transformation pathways can then be proposed.

Amorphization can be observed from the diminishing higher-order NN shells (in particular, second and third NN shells) from the FT of EXAFS as the order of atoms in the lattice becomes increasingly disordered. Since the data was collected at Ge edge, there were little or no signals from the second and third shells as cycling proceed. Therefore, N , R and σ^2 were determined for the first NN shell only for EXAFS analysis. Each *operando* set was fitted simultaneously with multiple k weightings (1 to 3) to reduce correlations among the fitting parameters. To further reduce the correlation between N and σ^2 for the *operando* data, the σ^2 values of Ge-Ge, Ge-Sn and Ge-Li scattering paths were fixed to 0.004, 0.003 and 0.01 respectively, which were the average of the σ^2 values for Ge-Ge, Ge-Sn and Ge-Li paths initially obtained from fitting each data. Similar to the pristine Sn-Ge (MS) samples, the S_0^2 value is 0.79 ± 0.04 , and was determined by fitting the pristine Ge powder. This value is kept constant in subsequent data fitting.

Chapter 4 Fabrication and Characterization of Melt spun $\text{Sn}_x\text{Ge}_{1-x}$

4.1 Introduction

Key criteria of next generation anode materials call for higher gravimetric and volumetric capacities as well as high rate capability. Higher capacities and better rate capability can easily be realized by i) choosing anode materials with inherent high theoretical capacities, ii) using the right strategies to prepare the materials, such as nanostructuring. However, volumetric capacity is dependent on tap density. For nanosize materials, tap density will be lower than micro size ones and thus result in lower volumetric capacity. In this work, a novel process is used to create micro size particles with unique microstructures that results in the formation of novel Sn-Ge alloy. Melt spinning is used to create Sn-Ge in thin flake like forms, which are then ground to sub-micron size to study the differences in Li storage properties as compared to pure Sn and Ge precursors of similar particle size (Appendix, Figure A1). Due to the effect of rapid solidification, the crystallites may not have sufficient time to nucleate and/or grow into bigger crystals, resulting in very small grain size and/or regions with short range order and possibly extension of solid solubility.

4.2 Microstructures of Melt spun Sn-Ge

After melt spinning, thin metallic-like flakes of ~ 1 cm long and 2 mm wide were obtained. Figure 16 shows the backscattered images representative of the Sn-Ge (MS) samples. The nomenclature of the MS samples from this point onwards of the discussion will follow the ratio of the precursors, e.g. 4:6 will mean Sn/Ge in the ratio of 4:6. In the cross sectional BSE images, the lighter regions are contributed by heavy elements while the darker regions are contributed by lighter elements. Figure 16 (a) and (d), which represents the melt spun sample with a starting precursor ratio of 6 Sn: 4 Ge, consists of dispersed dark-colored clusters in a light-colored matrix. As the Sn to Ge ratio is increased towards higher Ge content, the dark-colored clusters grew in size (Figure 16 (a) - (f)) and ultimately becomes the main phase, with light-colored regions forming boundaries around them (Figure 16 (c) and (f), Sn:Ge ratio of 2:8). Such distinct contrasting regions are unique to rapidly quenched alloys, and indicate two possibilities, i) Sn and Ge are immiscible in each other, resulting in phase separation; or ii) extended solid solution is formed. From the phase diagram of Sn-Ge (Figure 17), under thermodynamically equilibrium conditions, Sn exhibits very low miscibility of < 1 at. % in Ge. The high immiscibility of Sn in Ge is due to the large difference in atomic sizes between these two elements. Therefore under thermodynamically equilibrium conditions, Sn and Ge are unlikely to form alloys or solid solutions at such high Sn concentration. However, rapid solidification processes with cooling rate higher than 10^3 K/s are known to impart extraordinary properties, i.e. extension of solid solubility, formation of metastable crystalline and amorphous phases.^{116, 118} To gain insights and understanding of how the elements are distributed, the phase-compositions as well as grain size of the Sn-Ge (MS) materials, EMPA and TEM were used.

Figure 16 Cross-sectional BSE images of (a, d) 6:4, (b, e) 4:6 and (c, f) 2:8.

Figure 17 Phase Diagram of Sn-Ge.¹¹¹

4.3 Phase Identification and Analysis

4.3.1 Electron Probe Micro Analysis

Under equilibrium conditions Sn is highly immiscible in Ge, even if some amount of Sn did become miscible with Ge, the resolution of energy dispersive X-ray (EDX) technique of mapping compositional distribution may be inadequate in detecting it. Herein, EMPA with resolution good to a few hundred nanometers was used to map out the compositional distribution of Sn and Ge in the melt spun flakes made with various ratios of Sn and Ge.

The same samples used in BSE imaging were used in this instance to map out the compositional distribution of the melt spun flakes. Only Sn and Ge were detected, indicating that the samples prepared via melt spinning are free from contaminants. The distribution of Sn in the samples is presented in gradient maps and plotted statistically the overall distribution of Sn in the samples (Figure 18). Only Sn maps are shown for clarity purpose. The statistical distribution of Sn, as shown below each of the geochemical map corresponds well with the amount of Sn use in the starting precursor. When the starting precursor Sn:Ge ratio is 6:4, Sn exists mostly in its pure form (in pink) with small clusters that are mapped in green or blue, containing a mixture of Sn and Ge. As the amount of starting precursor is increased to higher Ge content, i.e. Sn:Ge ratio is 4:6, the area of the pink regions decreased considerably, while the blue regions increased significantly. This indicates that the amount of Sn existing in pure Sn element form decreases and most of the Sn exists together with Ge, forming a Ge-rich phase. When the starting precursor Sn:Ge ratio is further tuned to 2:8 (Ge-rich),

the area occupied by pure Sn decreased drastically, indicating the possibility that most of the Sn are in the Ge-rich phase. Recalling that the Sn-Ge (MS) samples were prepared from a thermodynamically non-equilibrium process, it is possible that the solid solubility has been extended. From EPMA mappings, it suggests that Sn is forming Ge-rich alloy with Ge.

(a)

(b)

(c)

Figure 18 Geochemical maps of samples with Sn:Ge ratio of (a) 6:4, (b) 4:6 and (c) 2:8.

HRTEM was used to gain insight into the atomic structure of the melt spun Sn-Ge. A representative HRTEM image for Sn-Ge (MS) is shown in Figure 19. Regardless of the composition of Sn-Ge, at the atomic level, the features are similar, i.e. highly crystalline grains of 5 – 20 nm. The nanocrystalline grains are a result of rapid solidification. As a result of the high cooling rate, the crystals have time to nucleate but insufficient time to coalesce and grow. The inset selected area electron diffraction (SAED) pattern shows the polycrystalline nature and attests to the good crystallinity of the sample. According to the Gibbs-Thomson effect, nanocrystalline materials have been demonstrated to exhibit enhanced solute solubility even if they are conventionally of immiscible nature.¹³⁴ Hence, extended solubility of Sn-Ge may be induced by the fine nanocrystalline grains of < 10 nm that has resulted from the MS process (Figure 19). To further investigate and gain a deeper understanding on the degree of extension of solubility, the XRD data are modelled and fitted via Rietveld refinement to extract useful information regarding the crystal structure and phases formed. These data are then correlated to experimental evidences from Raman spectroscopy and EXAFS to provide a complete picture to the constituent phase(s) of these novel Sn-Ge materials.

Figure 19 Representative HRTEM image of pristine Sn-Ge (MS).

4.3.2 X-ray Diffraction and Rietveld Refinement

The XRD patterns of the melt spun Sn-Ge of various ratios are as shown in Figure 20. All the XRD peaks can be attributed to β -Sn and Ge (PDF 00-004-0673 and 00-004-0545) and no impurities phases are detected. However, Ge peaks are observed to become broader and shifted to lower 2θ as the amount of Ge in the sample decreases (Figure 21). Peak shift and broadening can be due to a number of factors such as change in lattice parameters, reduction of crystallite size etc. Rietveld refinement was performed for each dataset to gain insights into the samples prepared via MS process. The XRD patterns were fitted to β -Sn and Ge (PDF 00-004-0673 and 00-004-0545) respectively, suggesting that the crystal structures of the phases formed are in the native tetragonal structure β -Sn and diamond cubic Ge. The results of the refinements are presented in Table 2. From the table, the lattice parameters of Sn undergo minimal

changes and are well within uncertainty errors. It can thus be assumed that Ge atoms did not enter the lattice of Sn and that these Sn can be accounted for as unreacted β -Sn phase. On the other hand, Ge lattice parameter underwent drastic increase as the concentration of the starting Sn precursor increases. The lattice parameter, a , increases from 5.623 Å in pure Ge to 5.899 Å in melt spun samples with starting precursor Sn:Ge ratio of 7:3. This distortion of the lattice implies that some Sn may have entered the Ge lattice either as interstitials or replacing some Ge atoms, causing expansion of the lattice due to the larger atomic size of Sn atoms. The sharpness of the peaks in the spectra suggests that the crystallite size may be larger and cover a wider range of distribution than what was observed in HRTEM images. HRTEM is a highly localized imaging technique whereas XRD can provide a broad overview of the average crystallite size. By nature of XRD technique, the average size calculated from the line width is volume-weighted, while in TEM, it is number-weighted. The grain size determined by TEM is thus, typically much smaller than those determined by XRD. This is to a large extent, due to differences in the weighting of the “average”.

As shown in Table 2, the average crystallite size of β -Sn phase in the MS samples are relatively constant in the range of ~ 50 - 60 nm, unaffected by rapid solidification. On the other hand, MS process has a drastic effect on the Ge-rich phase, whereby the crystallite size decreased with the increased in Sn concentration. Overall, the crystallite sizes of the pure β -Sn phase in all Sn-Ge (MS) samples, and Ge-rich phase of 1:9, 2:8 samples are larger than that observed from HRTEM image. Also, on first look the composition as determined from Rietveld refinement analysis appear to

deviate greatly from the initial starting precursor ratio, with a surplus of Ge. The reasons for the deviation will be highlighted in details in Section 4.3.4.

Figure 20 XRD patterns of melt spun Sn-Ge with different Sn:Ge ratios.

Figure 21 Peak shift and broadening with reduced Ge concentration.

Table 2 Phase composition and lattice parameters extracted via Rietveld refinement.

Sample	Sn			Ge-rich phase		
	At. % Sn	Lattice Parameters (Å)	Crystallite Size (nm)	At. % Ge-rich	Lattice Parameter (Å)	Crystallite Size (nm)
Sn	100	a = 5.830; c = 3.181	185.2	-	-	-
7:3	60.1	a = 5.833; c = 3.183	56.0	39.9	a = 5.899	6.2
6:4	36.6	a = 5.831; c = 3.181	53.1	63.4	a = 5.763	13.8
4:6	31.5	a = 5.830; c = 3.181	50.2	68.5	a = 5.716	13.5
2:8	14.1	a = 5.828; c = 3.180	61.8	85.9	a = 5.689	31.5
1:9	7.9	a = 5.827; c = 3.179	60.6	92.1	a = 5.665	53.0
Ge	-	-	-	100	a = 5.623	287.2

4.3.3 Raman Spectroscopy

From XRD, one can only observe peak shift which is related to expansion of the lattice and thus, postulate and infer that the expansion may be due to the introduction of Sn in Ge lattice, since the expansion is detected in Ge data. However, to conclude if some novel Sn-Ge alloy has formed, the local structure of the lattice needs to be characterized. Raman spectroscopy was used to provide spectroscopic evidence for the existence of the $\text{Sn}_{1-x}\text{Ge}_x$ alloy by probing the local bonding environment of Sn-Ge (MS) (Figure 22). Pure Ge has a characteristic longitudinal optical (LO) phonon peak at 301 cm^{-1} , distinctive of the Ge-Ge phonon mode. In Sn-Ge (MS) samples, a broad band Ge-Ge peak dominates but is downshifted substantially as Sn content increases. This is due to a combinatory effect of mass difference between the constituent atoms, i.e. Sn and Ge as well as bond stretching when Sn is incorporated into Ge.¹³⁵ It has been reported previously in the literature that for Sn-rich Sn-Ge alloy, the Sn-Ge phonon mode is observed at 220 cm^{-1} . Therefore, for alloy with increasing Ge content, the Sn-Ge band is expected to shift to higher frequency but below that of Ge LO phonon peak.¹³⁰ Consequently, the weak shoulder peak observed at 241 cm^{-1} and 267 cm^{-1} in the melt spun samples can be assigned to the Sn-Ge phonon mode. The downshift of wavenumber is associated with the amount of Sn that was incorporated into the Ge lattice. The more Sn being incorporated into the Ge lattice, the more the downward shift, i.e. due to longer bond distance. The observation of this additional weak peak provides strong spectroscopic evidence for the presence of tetrahedral Sn-Ge coordination and supports the hypothesis of the formation of an extended random Sn-Ge alloy.

Figure 22 Raman spectrum for Sn-Ge (MS). The spectra have been smoothened for clarity.

4.3.4 EXAFS Fitting on Pristine Sn-Ge (MS)

By performing a FT on EXAFS data, one can determine both qualitatively and quantitatively, the types of atomic interaction present in the sample, as well as parameters such as bond lengths and σ^2 , since the FT data depicts the real-space NN shells (typically up to 5 Å) in the sample. The EXAFS σ^2 is the variance in the absorber-scatterer distance, and are contributed by thermal vibrations and static disorder from local defects and surface effects. Since temperature is kept at room temperature throughout the XAS measurements, the contribution to σ^2 is mainly due to static disorder. For XAS, both pristine Ge and Sn-Ge (MS) samples were measured to understand the degree of change in the local bonding environment of Sn-Ge (MS).

Figure 23a shows the FT magnitude of EXAFS data as a function of distance in angstroms (Å) for pristine Ge and Sn-Ge (MS) samples. The intensities of the first, second, and third NN shells are observed to decrease with increased Sn concentration. This indicates that Sn is being incorporated into the Ge lattice and form Ge-Sn bond with the Ge atoms in the lattice. Also, the amount of Sn incorporated increased with the increased in Sn content. As the bond distances of Sn-Ge and Ge-Ge are different, electrons scattered from Ge to NN Sn and back to Ge are not in phase with the electrons scattered from Ge to NN Ge and back to Ge, thereby canceling out some of the FT magnitude contributed by Ge-Ge. The more Sn atoms incorporated in the Ge lattice, the greater the decrease in FT magnitude.

EXAFS fitting was carried out to extract quantitative information on pristine Ge and the Sn-Ge (MS) alloys. For pristine Ge, a diamond cubic Ge model (space group 227) is used in its fitting. For Sn-Ge (MS) samples, a good fit is achieved with a Ge-rich $\text{Ge}_{1-x}\text{Sn}_x$ alloy model, where Sn atoms substitute for some Ge atoms in the diamond cubic structure (Appendix Table A1). A typical fit on a Sn-Ge (MS) alloy is shown in Figure 23b. The scattering paths incorporated in the diamond cubic Ge model are one Ge-Ge path for each of the first, second, and third NN shells, and for the $\text{Ge}_{1-x}\text{Sn}_x$ alloy model, one Ge-Ge and one Ge-Sn path for each of the first, second, and third NN shells. The atomic percent of Sn obtained from the $\text{Ge}_{1-x}\text{Sn}_x$ alloy model and the corresponding atomic percent of Sn incorporated into the Ge lattice are presented in Figure 23c. It is clear that the higher Sn:Ge ratio alloys have higher percentage of Sn in the $\text{Ge}_{1-x}\text{Sn}_x$ alloy model, which indicates that there are more Ge-Sn bonds present,

as supported by Figure 23a. The corresponding atomic percent of Sn that is incorporated into the Ge lattice range from 7 – 11 at. % within error bars. This shows that the solid solubility of Sn in Ge has been extended by the MS process and that the alloy formed will contain more Sn if a high Sn:Ge ratio is used for the starting precursor. The fitted EXAFS data of the Ge-rich alloy phase can then be correlated to the phase composition from Rietveld refinement. As shown in Table 2 previously, the amount of Sn and Ge as determined from Rietveld refinement does not correlate well with the amount of starting precursors used. However, we have now learned from EXAFS fitting that some amount of Sn substituted for Ge in the Ge-rich phase. Thereby, the total amount of Sn (both unreacted and those that alloyed with Ge) and hence, the actual amount of Ge in the system can be determined. The results are shown in Table 3 and suggest that some of the starting precursors are lost in the course of MS processing, e.g. still remains in the tube. Samples with Sn:Ge ratios of 1:9 and 6:4 are the ones with the most deviation with 6:4 showing significant losses in Sn, indicating MS process parameters need to be further refined to obtain just the alloy phase.

Figure 23 (a) Fourier-transformed k^2 -weighted EXAFS for pristine Ge and Sn-Ge (MS) with different Sn/Ge ratio. (a) A typical EXAFS fit for 2:8 (MS) sample. (a) A plot of atomic percent Sn in $\text{Sn}_x\text{Ge}_{1-x}$ and atomic percent Sn incorporated into Ge lattice.

Table 3 Corrected phase composition of Sn-Ge (MS) after correlating Rietveld refinement and EXAFS fitting data.

Sample	At. % Ge – rich phase	At. % of Sn in Ge	At. % Sn Unreacted	Actual At. % Sn in Sample	Actual At. % Ge in Sample
1:9	92.1	8.1	7.9	16.0	84.0
2:8	85.9	7.0	14.1	21.1	78.9
4:6	68.5	9.0	31.5	40.5	59.5
6:4	63.4	10.7	36.6	47.3	52.8

The respective bond distances and σ^2 values are plotted as a function of Sn/Ge ratio in Figure 24 to investigate the effect of the starting Sn precursor amount for Sn-Ge (MS) samples on the bond distances (Figure 24a) and σ^2 values (Figure 24b). The bond distances for the first, second, and third shells for Ge-Ge remain fairly constant (within the range of error bars) at around 2.45 Å, 4.00 Å, and 4.70 Å respectively. On the contrary, Ge-Sn bond distances are generally longer than Ge-Ge bond distances for all shells for Sn/Ge ratio ≤ 0.25 . As the ratio increases, it is observed that Ge-Sn bond distance for the second and third shells are similar or lower than that of Ge-Ge bond distance, and it could be an indication of higher distortion with increasing Sn in the Ge lattice. This is supported by the trend in Figure 24b, where a higher Sn/Ge ratio leads to a gradual increase in the σ^2 values, implying an increase in static disorder. This suggests expansion of the lattice of the Sn-Ge alloy relative to pure Ge, is also supported by the lower 2θ positions of the Ge-Sn peaks observed previously in the XRD patterns and larger lattice parameter compared to pure Ge as determined via Rietveld refinement (Figure 21 and Table 2). From the measurement results collected via XRD, Raman spectroscopy and EXAFS technique, we conclude that Sn-Ge (MS) consists of a mixture of extended solubility Sn-Ge alloy with some residual pure Sn phase.

Figure 24 (a) Bond distance and (b) σ^2 values for first, second, and third shells for Ge-Ge and Ge-Sn bonds, as a function of Sn/Ge ratio.

4.4 Conclusion: Novel Sn-Ge Alloys via Melt Spinning

In this chapter, novel Sn-Ge alloys have been fabricated via MS processing, which consists of a Ge-rich alloy phase and some amount of residual pure Sn phase. Sn-Ge (MS) samples exhibit unique microstructures as a result of rapid solidification, crystallizing as nano grains that are about 5 – 50 nm for the Ge-rich phase and is dependent on the starting precursors ratio, whereas starting precursors ratio has less effect on β -Sn phase ($\sim$ 50- 60 nm). XRD data shows a leftward shift to lower 2θ as the amount of Ge in the sample decreases, which may be due to lattice distortion as a result of incorporation of Sn into Ge lattice. Rietveld refinement shows that Ge lattice parameter increased drastically from 5.623 Å in pure Ge to 5.899 Å in melt spun samples with starting precursor ratio of 7:3. In order to determine if the solubility limit has been extended, local bonding environment of Sn-Ge (MS) was surveyed by spectroscopy methods, i.e. Raman spectroscopy and X-ray absorption spectroscopy. Both spectroscopy methods provide evidences for the presence of tetragonal Sn-Ge bonds. Drawing correlation from refinement fitting and EXAFS analysis, the solid solubility range of Sn in Ge was determined to be in the range of 7 - 11 at. % Sn and is dependent of the concentration of Sn in the starting precursor.

Chapter 5 Electrochemical Properties of Melt Spun Sn-Ge

5.1 Introduction

Due to the high cooling rate of the MS process, instead of observing a phase separated Sn-Ge mixture, solubility limit of Sn-Ge was extended. This result in the formation of new Sn-Ge alloy phase with various amount of Sn incorporated into Ge lattice that is dependent on the starting precursors' ratio and some amount of residual pure Sn phase. In this chapter, it will be demonstrated that the presence of the novel Sn-Ge alloy phase as well as its unique microstructure play critical roles in the lithium storage properties of Sn-Ge. Comparison is made between similar particle size Sn-Ge (MS), elemental Sn, Ge and physically blended mixture of Sn-Ge which mimics an immiscible mixture of Sn-Ge, to elucidate the differences and to gain new insights. *Ex-situ* X-ray diffraction and absorption spectroscopy studies, and complementary HRTEM are performed on electrodes at various state of charge/discharge in the 1st cycle to establish the structure-property relationship and to gain an understanding for the improved Li⁺ storage properties.

5.2 Li Storage Properties: Cyclability

Sn-Ge (MS) samples are assembled into half-cell configuration and cycled galvanostatically between 0.01 – 1.2 V, at a C-rate of 0.1C up to 80 cycles (Figure 25). Cycle stability of the Sn-Ge (MS) samples improved considerably when the amount of unreacted pure β -Sn phase is reduced. Stable capacity is observed initially for 7:3 (up to 18th cycles), but rapid capacity fading quickly set in at around the 20th cycle, as depicted by the steep change in discharge capacity. By extrapolation of the corrected phase composition data, around 50 – 60 at. % reacted pure β -Sn phase is estimated to be present in 7:3. Drawing inference from Figure 18a, 7:3 will likely resemble the microstructure of 6:4 which consists of a continuous Sn matrix with Sn-Ge alloy embedded. It is envisioned that during the initial cycling, the Sn-Ge alloy phase may be able to alleviate and accommodate the volume change, as depicted by the flat plateau region with little change in reversible capacity. As cycling proceed, the unreacted β -Sn phase which exists as nanograins may agglomerate and grow into bigger grains. Some forms of phase transformation may have also taken place in the Sn-Ge alloy phase. Collectively, these series of transformation and reaction may contribute to the rapid capacity fading that was observed from 19th cycle onwards. As the amount of unreacted Sn in the samples decreased, capacity fading became less severe and constant capacities can be sustained over more cycles. Significantly, the best cycle life and Li storage is achieved when the Sn:Ge ratios are 2:8 and 1:9, and contain 14.1 and 8.8 at. % unreacted pure β -Sn phase respectively as determined in Section 4.3.4. Both 2:8 and 1:9 samples possess good first Coulombic efficiency and high reversible capacity over 1000 mAhg⁻¹. The microstructure imparted by MS processing technique undergo phase inversion when Ge content is much higher than

Sn, i.e. Ge-rich alloy phase now forms a continuous matrix with Sn “decorating” the boundaries the alloy phase. Among the two samples, 2:8 has a higher first Coulombic efficiency of 85% as compared to 74% for 1:9. This difference may indicate that there exists an optimum Sn-Ge alloy phase to unreacted pure Sn phase ratio which will result in better Li storage properties, where aggregation and agglomeration of nanograins can be alleviated, yet at the same time ensure good electrons and ions transports.

Figure 25 Cycling performance of Sn-Ge (MS) with various Sn:Ge ratio at C/10 rate.

From Figure 25, the optimum Sn-Ge (MS) samples have been identified. The work from this section onwards will concentrate on uncovering and understanding the possible factors that give rise to the good Li storage properties and correlating these properties to Li storage performances. 2:8 will be the sample used in the comparison

due to good capacity retention. Comparison will be made between 2:8, pure Sn, pure Ge as well as a physically blended Sn/Ge mixture of the same atomic ratio. From this point onwards, to simplify the nomenclature, 2:8 from MS process and Sn/Ge mixture prepared via physical mixing will be known as 2:8 (MS) and 2:8 (PM) respectively.

Cycling performance of 2:8 (MS) are evaluated and compared with that of pure Sn, pure Ge, and 2:8 (PM) as shown in Figure 26. The samples are assembled in the half-cell configuration and cycled galvanostatically between 0.01 – 1.2 V, at a C-rate of 0.1C at room temperature as previously. 2:8 (MS) shows considerable improvement in terms of cyclability and capacity retention compared to the reference samples. As expected of micron-sized pure Sn and pure Ge particles, they undergo huge volume variation that resulted in the loss of mechanical integrity during lithiation/delithiation. In particular, pure Sn exhibits gradual decrease in capacity up till the 12th cycle, after which onset of rapid capacity fading leads to total failure of the electrode by the 20th cycle. The overall profile of pure Sn is similar to 7:3, but capacity of pure Sn is constantly fading from the 1st cycle onwards whereas for 7:3, it remains constant up to 18th cycle. This indirectly shows that the presence of Sn-Ge alloy phase plays a crucial role in maintaining cycling stability. Also, it is interesting to note that the pure Sn underwent less severe capacity fading during the first 12 cycles, as compared to the literature, which may be the results of using CNTs as conductive additive. The CNTs formed networks that encrusted the pure Sn particles within them, but with cycling, Sn particles agglomerate and grow in size and cracking of the electrode occurs which render poorer electrical contact between the Sn particles and the CNTs.¹³⁶ The increasing loss of electrical contact between conductive additives, Sn particles and current collector leads to rapid capacity fading that was observed to set in after the 12th

cycle.

Compared to pure Sn, capacity of pure Ge decreased at a slower rate from $\sim 1400 \text{ mAhg}^{-1}$ in the 1st discharge cycle to $\sim 600 \text{ mAhg}^{-1}$ by the 60th cycle, a 43% reduction in capacity. Pure Ge is more robust compared to pure Sn, which may be due to the difference in reaction mechanism and pathway as investigated by Jung *et. al.*¹³⁷ Similarly, the 2:8 (PM) sample exhibits inferior electrochemical properties relative to 2:8 (MS). The cycling profile of 2:8 (PM) resembles that of a hybrid between pure Sn and pure Ge, bearing characteristics of both elements. This is expected since 2:8 (PM) is a physically blended mixture of pure Sn and Ge powder, where individual characteristics of pure Sn and pure Ge are preserved. Despite having a higher first charge capacity of 1208 mAhg^{-1} and low first cycle irreversible loss of $\sim 20\%$, 2:8 (PM) undergoes a significantly faster capacity fading after ten cycles with 40% capacity retention (475 mAhg^{-1}) at the 60th cycle. Its capacity retention ($475 \text{ vs. } 600 \text{ mAhg}^{-1}$) is poorer as compared to pure Ge. This indicates that while having immiscible Sn and Ge entities helps to alleviate the effect of electrochemical sintering, it is only effective for the initial few cycles. After which pulverization becomes inevitable and prevalent due to the large particle size of Sn and Ge (Appendix A, Figure A1). In fact, faster capacity fading is observed when the system contains both Sn and Ge compared to pure Ge, as observed quantitatively from the cycling behaviour plot. Both Sn and Ge are known to undergo huge volume variation during lithiation/delithiation and given the particle size at which the study is being conducted at, cracking of the electrode upon prolonged cycling is unavoidable. Thereby, simple mixing of Sn and Ge will not be effective in relieving and accommodating strain since the volume expansion of both Sn and Ge are exceptionally large (200 – 300%) and the

effect is additional, thus overwriting the potential benefits of a stepwise reaction mechanism.

On the other hand, 2:8 (MS) sample attained high reversible capacity of 1056 mAhg⁻¹ that remains relatively stable throughout the 60 cycles with low irreversible first cycle capacity loss of 15% for (Figure 26). By alloying Sn with Ge changes the unit cell lattice parameters and intrinsically the bond distance between atoms. At the same time, the unique microstructure imparted by MS processing technique helps to prevent Sn from agglomerating, since phase is inversed as compared to high Sn content samples, i.e. Ge forms the matrix with Sn embedded within the matrix. Furthermore, the nano-sized grains can help to accommodate strain. Consequently, high reversible capacity of ~ 1000 mAhg⁻¹ is maintained over the 60 cycles measured with an average Coulombic efficiency of 98%.

Figure 26 Comparison of cycling performance of 2:8 (MS), 2:8 (PM) with pure Sn and Ge at C/10, over the 1st 60 cycles.

Electrode (Pressed) densities of the sample were measured from which the volumetric capacity can be determined and are presented in Table 4. The electrode density of 2:8 (MS) is determined to be almost thrice of pure Sn and twice of Ge and 2:8 (PM), at 1.51 gcm^{-3} . Its corresponding volumetric capacity is calculated to be 1591 mAhcm^{-3} at 0.1C, which is over three times that of the pure Ge and almost 13 times that of pure Sn. Alloying of Sn with Ge allows the packing of more electrode material per unit volume, which may result in lighter weight, higher Li storage batteries as compared to graphite.¹³⁸ This also indicates that at similar particle size, and despite the use of CNT as conductive additive to impart stronger structural stability, the inherent phase-structure properties of the materials play a deciding factor in the cyclability of the electrode.

Table 4 Experimental electrode density and corresponding volumetric capacity at 60th Cycle

Sample	Electrode Density (gcm^{-3})	Volumetric Capacity (mAhcm^{-3})
Ge	0.86	494
2:8 (MS)	1.51	1591
2:8 (PM)	0.77	366
Sn	0.39	20

5.2.1 Understanding Electrochemical Process of Sn-Ge (MS)

Differences in reaction mechanisms between 2:8 (MS) and the reference samples are observed from the 1st cycle voltage profile plot (Figure 27a). Voltage plateaus around 1.2 – 1.5 V were observed for all samples during lithiation at the first cycle. However, these plateaus are absent in the 2nd cycle (Figure 27b) and can thus be attributed to the

formation of solid electrolyte interphase (SEI) as a result of side reactions of solvent/electrolyte on electrode surfaces during the 1st cycle. Pure Sn and pure Ge samples are characterized by their representative multi-steps constant voltage plateaus in the voltage range of 0.30 – 0.78 V as they underwent the phase transformation from M (where M = Sn, Ge) to Li_yM ($y \leq 4.4$). These plateaus correspond to the different solid-solution regions wherein each plateau represents regions of the co-existence of two-phases of Li_yM during lithiation/delithiation with M.¹³⁹⁻¹⁴² 2:8 (PM) exhibits several distinct plateaus that correspond well to those observed in pure Sn and Ge. However, the overall profile of 2:8 (PM) more closely follows that of pure Ge due to the high Ge content (ratio of 4 Ge : 1 Sn) in the sample prepared.

On the other hand, the constant voltage plateau of 2:8 (MS) lies between that of pure Sn and Ge, at ~ 0.5 V. According to the thermodynamics of mixing, the alloy form from two elements will have potential that lies between that of the two elements.⁴⁶ The potential at which the voltage plateau occurs thus provides another indirect evidence for the presence of Sn-Ge alloy in 2:8 (MS) sample. During delithiation, instead of having another voltage plateau as observed in pure Ge (0.58 V) and 2:8 (PM) (0.56 V), a sloping curve is observed for 2:8 (MS) with increased in voltage. This is due to the small crystalline grains that resulted from the MS process and/or amorphization that may have occurred during delithiation. Such observations have also been reported in several Sn-based alloys anode systems, whereby distinct plateaus are absent and become sloped. This phenomenon was attributed to (i) the presence of amorphous phase(s) and/or (ii) the particle sizes are smaller than a critical value.¹⁴³

Figure 27 (a) 1st and (b) 2nd cycle voltage profile of 2:8 (MS), 2:8 (PM), pure Sn and Ge at C/10 rate.

As the lithiation/delithiation potentials of Sn and Ge lie in close proximity, especially around 0.4 V, it is difficult to distinguish the reaction sites from the voltage profiles and cyclic voltammetry profiles (Appendix A, Figure A3). The corresponding differential capacity plots for the first cycle are reconstructed from the voltage profiles, so that specific information on the reaction potential of the various species can be extracted (Figure 28). The presence of multiple sharp peaks that correspond to pure Sn and Ge in 2:8 (PM) suggests that the process follows the stepwise lithiation reaction typical of a two-component active/active system and do not differ much from the parent pure Sn and pure Ge profiles. On the other hand, broader peaks are observed for 2:8 (MS), which indicates the much smaller grain size of the phases present in MS as compared to the reference samples despite having similar particle size. Also, the peaks of Sn during lithiation are broadened and barely distinguishable apart. Upon delithiation, the peaks still remain broad, indicating that the grains did not agglomerate or aggregate into larger clusters after the 1st cycle.⁹⁹ The presence of fewer peaks during lithiation and broad peaks during delithiation for MS sample is believed to be beneficial for the improved cyclability as the electrode underwent fewer phase transformations and consequently, lesser degree of volume variation.

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Figure 28 First cycle differential capacity plots of Sn, Ge, 2:8 (PM) and 2:8 (MS).

5.3 Li Storage Properties: Rate Performance

The cycling performance of 2:8 (MS) is shown to be related to the alloy phase that was formed and the unique microstructure imparted by MS process in Section 5.2. In this section, the rate capabilities of various MS samples, pure Sn and pure Ge samples are measured at various current densities to elucidate its rate of lithiation/delithiation (Figure 29). The cell was cycled at various current densities, starting with 0.1C up to a maximum of 5C. As observed, pure Sn has the worse rate capability at all C-rate measured. Rate capability is improved with the increased in Ge concentration in the formulation. Pure Ge gave higher capacities up to 0.5C, after which 2:8 (MS) performs better at high C-rates. This may be attributed to the Sn-Ge alloy phase that is present. From the literature, Sn-Ge alloy will have higher carrier mobility due to a lower effective mass of the alloy as compared to Ge. The increased in carrier mobility implies the more efficient transportation of electrons.¹⁴⁴ For 2:8 (MS), high capacity of over 1000 mAhg⁻¹ is demonstrated at C-rates of 0.1C and 0.2C. At higher current densities, the capacities decrease to 960, 885 and 680 mAhg⁻¹ at 0.5C, 1C and 2C respectively. Importantly, a high capacity of 500 mAhg⁻¹ is attained at a very high C-rate of 5C (current density of 7.15 Ag⁻¹). The corresponding volumetric capacity at 5C is 1800 mAhcm⁻³, which is notably among the highest attained so far for anode materials at such high current density.^{106, 145} Overall, the capacities obtained by 2:8 (MS) at the various current densities measured are all higher than those obtained by graphite and surpass that of carbon coated Ge nanoparticles and Ge-graphene nanocomposite.^{23, 146} The improved rate performance over Ge is due to the interplay of the unique microstructure as well as the effect of alloying Sn in Ge as evident from the higher capacities at high C-rates. Such configuration not only minimizes pulverization

of electrode, but also shortens lithium diffusion pathways, allowing more efficient transport of Li ions throughout the electrode. Therefore, the good rate performances are the result of concurrent improvement of both ions and electrons transport. Overall, the capability to deliver high capacity at high C-rates makes Sn-Ge (MS) among the most favourable candidates for fast charge/discharge applications.

Figure 29 Rate capabilities of Sn-Ge (MS), pure Sn and pure Ge measured at C/10, C/5, C/2, 1C, 2C and 5C rates.

5.4 Correlating Li storage properties to structure-property relationship

Ex-situ XRD, XAS and HRTEM techniques were used to characterize 2:8 (MS) electrode material after the first cycle to establish the structure-property relationship and to gain an understanding for the improved Li^+ storage performance (Figure 30). *Ex-situ* XRD patterns that were collected at various cut-off voltages during first cycle lithiation/delithiation are shown in Figure 30a. The crystallite size and lattice parameters of Sn and Ge-rich alloy phases were obtained from Rietveld refinement of *ex-situ* XRD data, and the corresponding results are presented in Table 5. From Figure 30a, peaks that belong to Ge-rich alloy are observed to decrease in intensities during lithiation and only partially recovered upon delithiation to 1.2 V. The peaks continue to weaken in intensities as lithiation proceeds and peak broadening is observed upon delithiation, i.e. indicating that Ge remains in a highly amorphous form after the first cycle. The lattice parameter of the Ge-rich alloy phase is found to contract even at 1.57 V, which is way higher than the potential at which Ge transformed into Li-Ge phase (below 0.6 V). It is postulated that the contraction of lattice may possibly be due to the “liberation” of Sn from the Ge-rich alloy phase. By 0.14 V, Ge peak is almost indistinguishable and indicates the increased disorder in the Ge-rich alloy phase. The increased disorder is due to the transformation from crystalline to amorphous phase via ESA and have been investigated in the literature during the lithiation of Si and Ge.^{108, 109} On the other hand, crystalline Sn is not observed to have undergone ESA from current experimental results. Experimental data shows that Sn exists in the crystalline β -Sn phase at all cut-off voltages and was observed to decrease in size

during lithiation, except at low voltage (0.14 V) where it increased slightly in size. This may be due to the slight agglomeration of the small nanoparticles. Apart from the change in crystallite size for β -Sn, the peaks for β -Sn remain present throughout lithiation and delithiation. This may suggest that the Sn that was liberated from Sn-Ge alloy acts as buffers and did not take part in the reactions or that the Li_xSn phases are metastable and will revert back to Sn phase upon disconnection from the circuitry. Peaks belonging to Li-rich Li_xSn phases are also not observed, with similar observations reported in the literature.⁸ There are a few possible reasons for such observations. (i) Degradation of electrode phase-composition and/or artefacts may be introduced during the disassembly process, i.e. dynamic phases cannot be captured. (ii) The inherent limitations in the resolution of laboratory XRD coupled with high background to noise ratio renders the Li-rich Li_xSn phases undetectable. To gain a deeper understanding, in-situ experiments should be carried out to verify the results.

In order to confirm the hypothesis that Sn is liberated from Sn-Ge alloy and that the Ge that is left behind to take part in the lithiation/delithiation process has indeed become amorphous, EXAFS spectra for 2:8 (MS) were collected at the same lithiation/delithiation cut-off voltages as *ex-situ* XRD for the first cycle (Figure 30b). The FT peaks for Ge-Ge interaction for the first, second and third NN shells are observed to decrease with lithiation, as the incorporation of Li^+ into the lattice will cause the cleavages of Ge-Ge and Ge-Sn bonds. The absence of both the second and third shell NN shells towards the end of lithiation indicates an increase in disorder and gave a strong indication that the Ge-rich phase undergoes a crystalline-to-amorphous transition during lithiation. Upon delithiation to 1.20 V, the higher-order coordination shells did not recover, indicating that the sample has irreversibly become

amorphous after the first cycle. As observed in this work, ESA is an irreversible process and the structure remains in a highly disordered state upon delithiation.

In the case of SnSb alloy, they are structurally reversible, i.e. after Sn and Sb dealloyed with Li, SnSb alloy is reformed again towards the end of delithiation and was determined to be the key to enabling better reversibility. To investigate if the Sn-Ge alloy behave in a similar manner like SnSb alloy during delithiation, the first shell was fitted with the same Sn-Ge alloy model used in the fitting of pristine Sn-Ge alloy. The attempted fitting using the Sn-Ge alloy model showed that the percentage of Ge in the delithiated MS to be $\sim 103\% \pm 4\%$. Additionally, a negative σ^2 value is obtained for the Ge-Sn scattering path, indicating that the chosen fitting model is not suitable (Table 6). This implies that Sn-Ge bonds are unlikely to be present in the delithiated 2:8 (MS) sample. The delithiated 2:8 (MS) spectrum is then fitted with the Ge model (Table 6). The first shell coordination number is found to be ~ 2.2 . A comparison of the fitting with and without Ge-Sn scattering path is shown in Figure 31. Also, Li-Ge bond was found to be absent at the end of delithiation (1.2 V), as the incorporation of Li-Ge scattering path leads to a negative σ^2 (Table 7). This indicates that all the Li that alloyed with Ge during lithiation has been removed from the Ge lattice by the end of the delithiation process. The complete removal of Li from the Ge lattice is necessary to maintain high reversible capacities with low losses.

From the microstructure perspective, the HRTEM image shows that significant changes in microstructure have occurred after the first cycle delithiation process (Figure 30c). The microstructure now contains some crystalline grains, which have been identified as β -Sn and Ge, embedded in an amorphous matrix. The β -Sn may

have originated from the β -Sn that is initially present and/or formed *in-situ* as it precipitates out from the Sn-Ge alloy. The crystalline Ge detected may belong to the residual Sn-Ge alloy phase that has yet undergone ESA. Due to such microstructural transformation, the nanograins are being dispersed in an amorphous matrix, preventing their aggregation and agglomeration which is crucial in maintaining cycling stability.¹⁴⁷ The SAED pattern (Figure 30d) consists of faint polycrystalline rings and diffuse amorphous rings, confirming the presence of amorphous Ge (a-Ge), CNT and β -Sn. Due to the close proximity of the d-spacing of a-Ge and CNT, the diffuse amorphous rings of a-Ge appears to be smeared with those of CNT. These observations are in good agreement with the findings from *ex-situ* XRD and EXAFS. These experimental evidences suggest that 2:8 (MS) departs from the stepwise lithium alloying mechanism that is typical of active/active alloy, e.g. SnSb. Instead of expecting a structural reversible Sn-Ge alloy, an amorphous matrix of Ge with nano-sized crystalline β -Sn embedment results after the first cycle. It may be proposed that the Sn-Ge alloy phase in 2:8 (MS) undergoes an irreversible conversion process to produce β -Sn *in-situ*, and concurrently, ESA of Ge occurs that prevents the agglomeration of the crystallite phases. Differential capacity plots for the 5th and 20th cycles of MS suggest that there are no changes to the shape and intensity of the plots even after prolonged cycling (Figure 32). This indicates the good reversibility of such microstructural configuration of having an amorphous Ge matrix with crystalline β -Sn embedment upon repetitive cycling.

Table 5 Summary of crystallite size and lattice parameters of Sn and Ge-rich alloy phases at various cut-off voltages during the first cycle. Reproduced by permission of The Royal Society of Chemistry.¹⁰³

Cut-off Voltage (V)	Sn		Ge-rich alloy	
	Crystallite Size (nm)	Lattice Parameters (Å)	Crystallite Size (nm)	Lattice Parameter (Å)
Pristine	30.472	a = 5.828 c = 3.180	33.136	a = 5.699
1.57 (Lithiation)	28.156	a = 5.828 c = 3.181	15.479	a = 5.692
0.32	13.941	a = 5.816 c = 3.181	-	-
0.14	15.664	a = 5.825 c = 3.181	-	-
1.20 (Delithiation)	28.983	a = 5.830 c = 3.181	-	-

Figure 30 (a) *Ex-situ* XRD of lithiated/delithiated 2:8 (MS) samples at various cut-off voltages during the first cycle. (b) Fourier-transform of k^2 -weighted EXAFS for same 2:8 (MS) samples as (a). (c) HRTEM image of 2:8 (MS) after 1 cycle showing nanocrystalline Sn grains in a highly disordered matrix. (d) The corresponding SAED pattern. Reproduced by permission of The Royal Society of Chemistry.¹⁰³

Table 6 Summary of single-scattering paths used in the fit, and local structure parameters based on quantitative analysis of Fourier transforms of k^2 -weighted EXAFS spectra for delithiated 2:8 (MS) using the alloy model and Ge model. Uncertainties in the last digit(s) are given in parentheses. The percentage of Ge from the alloy model is refined to be $103\% \pm 4\%$. Notice that the σ^2 for alloy model is negative, indicating that the alloy model is not suitable for delithiated 2:8 (MS). Reproduced by permission of The Royal Society of Chemistry.¹⁰³

		N	R (Å)	σ^2 (10^{-3} Å ²)	Reduced χ^2 $\times 10^3$	R factor $\times 10^{-2}$
Alloy model	Ge-Ge	3	2.486 (30)	12.5 (30)	1.641	4.18
	Ge-Sn	1	2.457 (16)	-2.2 (38)		
Ge model	Ge-Ge	2.2 (4)	2.481 (11)	5.3 (14)	1.106	3.61

Figure 31 Fourier transforms of k^2 -weighted EXAFS spectra for delithiated 2:8 (MS) for the two fits. The fitting that includes both Ge-Sn and Ge-Ge bonds are represented by the red dots, and blue dots for the fitting with only Ge-Ge bonds. The dotted lines indicate the window used for the fit. Reproduced by permission of The Royal Society of Chemistry.¹⁰³

Table 7 Summary of single-scattering paths used in the fit, and local structure parameters based on quantitative analysis of Fourier transforms of k^2 -weighted EXAFS spectra for delithiated 2:8 (MS) for (i) where only Ge-Ge bonds are present, and (ii) both Ge-Ge and Ge-Li bonds are present. The negative σ^2 is an indication of the likely absence of Ge-Li bond. Uncertainties in the last digit(s) are given in parentheses. Reproduced by permission of The Royal Society of Chemistry.¹⁰³

Data		N	R (Å)	σ^2 (10^{-3} Å ²)	Reduced $\chi^2 \times 10^3$	R factor $\times 10^{-2}$
1.20 V (delithiation)	Ge-Ge	2.2 (4)	2.481 (11)	5.3 (14)	1.106	3.61
	Ge-Ge	2.0 (8)	2.469 (20)	1.2 (20)	1.772	4.82
	Ge-Li	0.14 (150)	2.719 (60)	-3.26 (50)

Figure 32 Differential capacity plots of 2:8 (MS) at 1st, 5th and 20th cycle. Reproduced by permission of The Royal Society of Chemistry.¹⁰³

5.5 Conclusions: Li Storage Properties of Sn-Ge Prepared by Melt Spinning Process

The Li storage properties of the Sn-Ge alloy prepared via MS process were examined with reference samples of similar particle size. As compared to elemental Sn/Ge and physically blended mixture of Sn/Ge, 2:8 (PM) in the same ratio as MS, 2:8 (MS) exhibits superior lithium storage performance over them. High and stable capacities of over 1000 mAhg^{-1} (1591 mAhcm^{-3}) were maintained over 60 cycles at a C-rate of 0.1C. Fast rate capability was also observed in 2:8 (MS), with capacities close to 1000 mAhg^{-1} , at C-rates up to 0.5C. Notably, capacity of 500 mAhg^{-1} (795 mAhcm^{-3}) was still attainable at a high rate of 5C. Also, the volumetric capacity 2:8 (MS) is notably among the highest reported to date for anode materials, making it a potential anode material for applications that require light weight, fast charging and high capacity. The enhancement may be attributed to the synergistic effect between the phases (importantly, the formation of the Sn-Ge alloy) and phase transformation that occurs during lithiation/delithiation. Based on the analysis from various characterisation techniques, it indicates that the Sn-Ge alloy deviates from the typical stepwise lithium alloying mechanism of active/active elements. Sn was liberated from Sn-Ge alloy, while simultaneously, Ge transformed from crystalline to amorphous state, before the usually Li alloying reactions occurred for Ge. Upon delithiation, Ge remained in amorphous form and did not transform back into crystalline form. The result is an amorphous matrix of Ge with nano-sized crystalline β -Sn embedded in it. However, only Ge and β -Sn phases were observable from *ex-situ* XRD and there lies several limitations in such techniques, limiting the true identification of the reaction mechanism.

From the differential capacity plots, the constancy of the plot indicates the good reversibility of the electrode material upon repetitive cycling. We postulate that having an amorphous matrix with dispersed nano-sized crystalline grains is a desirable configuration. As shown from both cycling and rate performance measurements, good cycling stability and rate capability can be achieved, in which large volume variation can be alleviated and pulverization reduced. The presence of short-ranged order and nanograins improved Li^+ transport efficacy by shortening the diffusion length of Li^+ , while the improved carrier mobility by alloying Sn in Ge facilitates more efficient electrons transportation. Furthermore, the use of CNT network as conductive additive helps to maintain structural integrity of the anode electrode and provides percolated electronic conduction network.

Chapter 6 Time Resolved *Operando* X-ray Studies of Melt Spun Sn-Ge

6.1 Introduction

From the previous two chapters, the phase(s) that resulted from MS process was determined and Li storage properties were characterized. The melt spun Sn-Ge materials were found to consist of a Sn-Ge alloy phase and some amount of residual elemental Sn. Generally, starting precursors with higher Sn content resulted in more residual Sn inside the melt spun product. The atomic percent of Sn in Ge was found to increase with increase in initial Sn concentration, and ranged from 7-11 at. % Sn. This indicated that the solubility limit of Sn-Ge has been extended via MS process. Among the Sn-Ge (MS) samples fabricated, the sample with Sn: Ge of 2:8 starting ratio gave the best Li storage properties, i.e. both cyclability and rate capability, due to a high concentration of Sn-Ge alloy in the sample and very little residual pure β -Sn phase, which will otherwise cause agglomeration of particles to occur within the first few cycles. Sample 2:8 (MS) was then examined using *ex-situ* X-ray methods at various cut-off voltages to gain an understanding for the improved lithium storage properties.

The enhancement in Li storage properties may be attributed to the synergistic effect between the phases (importantly, the formation of the Sn-Ge alloy) and phase transformation that occurs. Also, the *ex-situ* X-ray studies suggest that the reaction pathway of Sn-Ge alloy deviates from the typical stepwise lithium alloying mechanism of active/active elements. The Sn-Ge alloy undergoes a precipitation-alloying reaction, where Sn in the Sn-Ge alloy is observed to be liberated *in-situ* from the Sn-Ge alloy

phase to form β -Sn nanograins, while simultaneously, Ge transforms from crystalline to amorphous, before the usual Li alloying reactions occurs. Upon delithiation, the microstructure exists as nano-size Sn dispersed in an amorphous Ge matrix.

In this chapter, *operando* synchrotron X-ray studies were conducted on melt spun, physically mixed and pure elemental Sn and Ge samples to elucidate the reaction mechanism of Sn-Ge (MS). For this study, synchrotron X-ray diffraction and X-ray absorption spectroscopy are two practical methods chosen to complement each other. XRD will be able to provide insights into the crystalline phases that have formed and follow the phase transformation of these phases real time. Information on the lattice parameters and crystallite size can also be extracted. However, amorphous phases such as those that have resulted from ESA of Ge and the amorphous Li_xGe phases cannot be identified from XRD spectrum. Thereby, *operando* XAS can complement XRD technique by following the real time phase transformation of amorphous phases and to provide information on bond length to gain an understanding on the phase transformation that are occurring in the system. From which, a holistic picture on the reaction pathway of melt spun Sn-Ge can be painted. Unless otherwise stated, the following discussion will be based on data collected at C/10 rate.

6.2 Phase Identification

XRD spectra from the first two cycles were collected and analyzed. The full *operando* XRD spectra for 2 cycles of a typical melt spun sample used in this analysis can be found in Appendix Figure A4. All of the *operando* XRD spectra collected contain contributions from the polymer pouch as marked by ‘*’ as well as Li and Cu as denoted in the figures in Appendix A. The phases present in typical Sn-Ge *operando* XRD spectra have been identified as diamond cubic Ge (PDF 00-004-0545), β -Sn (PDF 00-004-0673), Li_2Sn_5 (PDF 01-074-0561), LiSn (PDF 03-065-1261), $\text{Li}_{15}\text{Ge}_4$ (PDF 00-089-3034). However, Li-rich Li_xSn phases can only be identified collectively by the hump that appears in the range of $Q = 2.65 - 2.70$ due to the lack of long range order in these phases.⁹²

6.3 Understanding Phase Transformation of Sn-Ge Alloy

From the previous *ex-situ* studies, it appears that Sn-Ge alloy will first undergo a “precipitation” reaction, in which Sn and Ge disintegrate into elemental entities before Li alloying with Sn/Ge occurs. In order to gain a deeper understanding about this phase transformation and reversibility of Sn-Ge alloy, Ge-rich alloy/Ge phase of the samples are analyzed. Figure 33 depicts the change in the amount of crystalline Ge with voltage as lithiation proceeds during the 1st cycle. Overall, across the samples, crystalline Ge phase is no longer observed by around 0.15 V. However, the origin where the amount of crystalline phase starts diminishing is different among the MS samples. In particular, the amount of crystalline Ge phase starts decreasing just below 0.4 V for 6:4 (MS) as compared to ~ 0.28 V for the other samples. Such early onset may be related to the larger amount of β -Sn and lower Ge ratio in the Sn-Ge alloy

which speed up the kinetics, leading to faster liberation of Sn from the Sn-Ge lattice. More work needs to be done to understand the kinetics. After the 1st lithiation, peaks belonging to Ge are no longer observed in the 1st delithiation, 2nd lithiation and 2nd delithiation spectra (Figure 34a – d).

Figure 33 The amount of crystalline Ge phase as a function of voltage during 1st cycle lithiation.

Figure 34 (a) Ge peak disappeared at ~ 0.16 V during 1st lithiation and did not recover during (b) – (d) 1st delithiation, 2nd lithiation and 2nd delithiation. Peak marked with ‘*’ is unidentified and may be contribution from some side reactions.

The lattice parameters of the samples were extracted from the 1st cycle lithiation XRD spectra and plotted as a function of voltage in Figure 35. Pure Ge and 2:8 (PM) bear similar resemblance with lattice parameters of 5.643 Å and 5.660 Å respectively. The slight deviation of 2:8 (PM) from pure Ge is unlikely to be due to the formation of solid solution since grinding of the precursors was completed within 1 min using mortar and pestle. The slight deviation may be a result of experimental error due to equipment and calibration. On the other hand, the melt spun samples showed

enlargement of lattice, with 6:4 (MS) having a larger lattice parameter (5.756 Å) as compared to 2:8 (MS) (5.695 Å) and pure Ge (5.643 Å) due to the incorporation of more Sn into Ge lattice as determined previously in Section 5.4. For 6:4 (MS), the point at which its lattice parameter starts to contract corresponds well with the origin of the decrease in the amount of crystalline Ge in 6:4 (MS) (Figure 33). This origin can be indexed to the broad peak in the differential capacity plot shown in Figure 36. The contraction in lattice parameter provides an indication and possibility that Sn is being “liberated” from the lattice of Sn-Ge alloy phase. Compared to 6:4 (MS), the lattice parameter of 2:8 (MS) only undergoes slight decrease below 0.19 V, and can possibly be due to the presence of fewer Sn-Ge bonds in the Sn-Ge alloy phase of 2:8 (MS), as determined previously in Section 4.3.4. Reasons for such observations are currently unknown and requires further investigations. Notably, even with the liberation of Sn from the lattice, the lattice parameter are still slightly bigger than pure Ge. This may be due to residual dangling bonds or incomplete liberation of β -Sn from the Ge lattice.

Figure 35 (a) Lattice parameters of Ge-rich phase extracted from Ge (111) peak. (b) zoomed in showing the change in lattice parameter of Sn-Ge (MS) samples.

Figure 36 Differential capacity plot of Sn-Ge (MS) samples and pure Ge during 1st lithiation.

To further investigate and correlate the contraction of lattice to the absence or presence of Sn-Ge bonds, fitting of Fourier transformed EXAFS spectra were carried out. From the fitting, the coordination number and the bond distance of the nearest neighbor of Ge and Sn atoms can be determined quantitatively. Briefly, each data set was first fitted with both Ge-Ge and Ge-Sn shells. Subsequently, for data measured below the first phase transformation of Ge at ~ 0.283 V, a Ge-Li shell was added. The relationships between the EXAFS parameters (bond distance and coordination number) and the differential capacity plot for 1st lithiation are shown in Figure 37a and 37b, respectively. In the beginning of lithiation, the fits are realized using the Ge-rich $\text{Ge}_{1-x}\text{Sn}_x$ alloy model with 1 Ge-Ge shell and 1 Ge-Sn shell, indicating that the electrochemical reaction has yet to take place significantly and the sample still behaves very much like in a pristine state. However, as lithiation processed to below $\sim$

0.283 V, the Ge-rich $\text{Sn}_x\text{Ge}_{1-x}$ alloy model gives poor fitting. This can be observed from the absence of Sn-Ge interaction from this point onwards (Figure 37a), and indicates that Sn-Ge bonds have been broken to liberate Sn atoms *in-situ*. This is in close agreement with the observation of the change in 6:4 (MS) lattice parameter, where the lattice parameter started to decrease before the onset of the first Ge lithiation peak (Figure 35b). From lattice parameter point of view, the lattice parameter of 2:8 (MS) may have reached the “ideal” state, wherein the liberation of Sn from Ge does not cause much structural distortion to the lattice, and yet the effect is observable from EXAFS fitting.

For fitting below 0.283 V, a good fit can only be obtained with a 1 Ge-Ge shell and 1 Ge-Li shell, indicating that Sn-Ge bond concentration may be beyond detection limits, i.e. breaking of Ge-Sn bonds. Due to a lack of intensity in the FT, the data collected below ~ 0.1 V could not be fitted satisfactorily. As the Ge-Sn bond ($230.1 \text{ kJ mol}^{-1}$) is weaker than Ge-Ge bond ($264.4 \text{ kJ mol}^{-1}$), Sn-Ge bonds breaking will occur before Ge-Ge. The coordination of Ge-Ge starts to decrease gradually after the disappearance of Sn-Ge bond, suggesting an increase in disorder, i.e. the onset of ESA. Therefore, by drawing correlation from both techniques, it can be seen that the contraction of lattice is related to the liberation of Sn atoms from Ge lattice and occurs before the onset of ESA and alloying of Li with Ge. This may also suggest that Sn-Ge alloy itself is electrochemically inert and that *in-situ* liberation of Sn atoms from Ge lattice first needs to occur before the usual Li alloying reactions can proceed. Also, an important observation is that, the Sn atoms are liberated at 0.283 V, meaning that the newly liberated β -Sn species will have to compete with existing Li_xSn , α -Ge and Li_yGe phases for Li ions during lithiation. This may result in some unlithiated species or “unlithiated core – lithiated shell”

configuration among the species due to the differences in diffusion rate through the various species and medium.^{148, 149} Such phenomenon when exists in a small and controlled manner, may help to ease the stress/strain related to excessive volume expansion.

Figure 37 (a) bond distances and (b) coordination numbers for Ge-Ge, Ge-Sn and Ge-Li bonds used in EXAFS fitting for lithiation. The graphs are overlaid on differential capacity plots for comparison purpose. EXAFS fitting on the FTs could not be carried out satisfactorily for data measured below 0.231 V, due to low backscattering intensities of the FT.

In order to gain insights on the reversibility of Ge, the Ge K edge X-ray absorption near-edge structure (XANES) was examined. XANES depicts the electronic transition from $1s$ to $4p$ electronic orbitals in Ge, with the intensity of the white line indicating the concentration of Ge $4p$ holes. A decrease in white line intensity indicates a decrease in concentration of $4p$ holes due to $3d$ - $4p$ orbital mixing from structural distortion in Sn-Ge alloy lattice, and/or phase transformation. In Figure 38, we see that the white line intensity (depicted on the y-axis as normalized absorbance) decreases with lithiation, indicating a higher level of disorder and phase transformation. Upon delithiation, there is an increase in the white line intensity upon delithiation, indicating that there is some recovery of the concentration of the Ge $4p$ holes.

Figure 38 Normalized operando Ge K edge spectra for lithiation and delithiation. The red spectrum represents the start of the delithiation cycle.

Figure 39 presents the first-derivative peak energies of the XANES spectra. The position of the first-derivative peak for the XANES spectra is related to the average oxidation state of Ge, where a peak at higher energy indicates higher oxidation state. Initially, the oxidation state of Ge remains the same as its pristine state at 11103 eV, but the peak starts to shift to lower energy as lithiation proceeds. The shift of the first-derivative peak to lower energy is due to the incorporation of lithium to the Ge-Sn lattice forming an amorphous Li-Ge phase, which provides an electron-shielding effect on the Ge atoms, and hence lowering the energy required to excite the Ge electrons from $1s$ to $4p$ states. As delithiation takes place, the 1st derivative energy slowly increases to a value of 11102.7 eV at the end of delithiation at 1.2 V. The 1st derivative XANES energy at the end of delithiation was recovered to almost the same value as pristine state. This is an indication of its high reversibility during electrochemical lithiation/delithiation.

Figure 39 1st derivative XANES peak energy for first electrochemical cycle

The FT of the EXAFS spectra was investigated to further understand phase transformation of Ge (Figure 40). The intensities of the first, second and third Ge-Ge shells for both 2:8 (MS) and Ge are observed to decrease as lithiation proceeds. Upon delithiation, only the first shell intensity underwent partial recovery. The higher-order shells did not recover, showing that the Ge lattice has become amorphous by the end of the electrochemical cycle. The first Ge-Ge shell of 2:8 (MS) underwent a 76.2% recovery as compared to 27.6% for pure Ge. This may indicate the improved reversibility of melt spun sample and/or there are now more Ge atoms available, i.e. after liberating from Sn-Ge alloy. This observation confirms our *ex-situ* XRD and XANES results in Chapter 5.

Figure 40 Evolution of Fourier Transform of Ge K edge EXAFS spectra of (a) pure Ge and (b) 2:8 (MS) during lithiation and delithiation. The red and yellow spectra indicates the delithiation process of Ge and 2:8 (MS) respectively.

6.4 Understanding Alloying of Li with Sn in Melt Spun Sn-Ge

In contrary to Ge, Sn did not undergo ESA. During the 1st lithiation, the intensity of Sn peaks started decreasing rapidly at ~ 0.43 V and vanished at 0.34 V (Figure 41 and 43a). Upon delithiation, the Sn peaks resurfaced at ~ 0.79 V and vanished at 0.53 V during the 2nd lithiation cycle (Figure 41, 43b and 43c). The peaks resurfaced again at 0.79 V during 2nd delithiation cycle (Figure 41 and Figure 43d). This shows the difference in phase transformation mechanism in β -Sn as compared to Ge and Si. Crystalline β -Sn is recoverable whereas the amorphization of Ge and Si are irreversible. Also, this may suggest the reason for the more rapid capacity fading as observed in the literature for β -Sn as compared to Ge and Si. The phase transformation of β -Sn as observed *operando* via synchrotron XRD (Figure 43) are found to deviate from that depicted in Figure 30, i.e. the spectra captured via ex-situ measurements. This discrepancy arises as a result of the limitations of *ex-situ* technique. Among which, the degradation of electrode phase-composition and/or artefacts that may be introduced during the disassembly process will lead to inaccuracy in the data. Dynamic phases may not being captured as intended, e.g. the persisting Sn peaks captured by ex-situ technique may be due to the degradation of Li_xSn phases. On the other hand, as *operando* synchrotron XRD is a real time technique, the measurements are captured as cycling of the cell proceeds without disassembling the cell/disturbing the environment of the cell and thus capture a more accurate picture of the ongoing reactions.

Looking at the crystallite size of the β -Sn that was recrystallized *in-situ* during delithiation, the size remains relatively constant between the 1st and 2nd delithiation process (Table 8). This shows that the crystallite β -Sn that was reformed *in-situ* were well dispersed and did not agglomerate. In the work by Fan *et. al* on time resolved *operando* X-ray study of micro-sized Sn, it will be shown that the accumulation of residual Li_2Sn_5 and LiSn phases that affect the reversibility of β -Sn electrode materials.¹⁵⁰

Figure 41 Amount of Sn in 2:8 (MS) as a function of voltage during cycling.

Figure 42 Differential capacity plots of Sn-Ge (MS) samples and pure Sn during 1st lithiation.

Figure 43 Reversibility of crystalline β -Sn phase as observed during *operando* XRD during (a) 1st lithiation, (b) 1st delithiation, (c) 2nd lithiation and (d) 2nd delithiation.

Table 8 Crystallite size of Sn during lithiation/delithiation from *operando* XRD

Sample	Pristine (nm)	1 st Delithiation (nm)	2 nd Lithiation (nm)	2 nd Delithiation (nm)
Sn	200.3	30.9	-	26.5
6:4 (MS)	30.9	27.2	-	25.6
2:8 (MS)	35.8	31.7	-	30.2
2:8 (PM)	55.2	59.9	-	58.0

Among the Li_xSn phases formed, Li_xSn with $x \leq 1$ reside in the crystalline form, while Li-rich phases of Li_xSn have been suggested to form short-range ordered structures at room temperature, due to low mobility of the atoms.⁹² Therefore, Li-rich Li_xSn phases can only be identified as a group based on their sublattice cell. From the XRD spectra, Li_2Sn_5 and LiSn can be identified and indexed, whereas for Li_xSn (where $x > 1$), it can only be characterized by the hump at in the Q range of 2.65 – 2.70. Peak area of Li_2Sn_5 is plotted as a function of voltage in Figure 44. It can be seen that there are some residual Li_2Sn_5 by the end of 1st delithiation for pure Sn, 2:8 (PM) and 6:4 (MS). This signifies the incomplete removal of Li from the Sn lattice that may arise from the sluggish kinetics of Sn.¹³⁷ On the other hand, 2:8 (MS) shows better kinetics, showing no residual Li_2Sn_5 . It may be postulated that the presence of some of the unlithiated species, e.g. Sn liberated during lithiation for the Sn-Ge (MS) samples provides additional pathway for improved transportation of Li^+ ions and hence, more effective removal of Li from the Sn lattice during delithiation. Therefore, as compared to pure Sn and 2:8 (PM), 6:4 (MS) has lesser amount of residual Li_2Sn_5 , whereas in 2:8 (MS), all Li atoms were removed from the system by the end of the first cycle and very slight amount of residue is observed in the 2nd cycle.

Correlating the normalized capacity contribution, which represents the lifetime of the species during lithiation/delithiation, for 1st and 2nd cycles (Figure 45) and peak area (Figure 44), one can see that despite the constant peak area of Li_2Sn_5 in pure Sn, its capacity contribution is actually on the decline. This implies that despite similar amount of Li_2Sn_5 being formed, not all of them contribute to capacity. In this context,

the capacity contribution is determined from the instance the Li_2Sn_5 peak starts forming in the *operando* XRD spectrum to the point it disappears, i.e. the lifetime of Li_2Sn_5 species. The capacity for 1st lithiation is then normalized to one and capacities at subsequent delithiation/lithiation is the relative capacity with respect to that of the 1st lithiation. This implies that the connectivity between the electrode materials and current collector may be broken, e.g. large scale cracking, which impedes electrons transport and render some of the Li_2Sn_5 phase inactive. For 2:8 (PM), capacity contribution of Li_2Sn_5 in the 2nd lithiation cycle were recovered to ~90% of the initial capacity. A synergistic effect due to the mixing of Sn and Ge and presence of amorphized Ge may help in the recovery by providing a percolated pathway for electrons transport and also keeping the β -Sn phase dispersed.

Interestingly, 6:4 (MS) and 2:8 (MS) show capacity contribution of over 1 for the 2nd lithiation, indicating capacity contributions that is greater than the 1st lithiation. Also, based on previous learning in Section 6.3, some of the Sn liberated from Ge lattice during 1st lithiation may remain unlithiated; only taking part in the Li-Sn alloying reaction during the 2nd lithiation cycle, which explains the origin of the increase in capacity contribution for the MS samples at 2nd lithiation. However, at 2nd delithiation cycle, 2:8 (MS) shows better reversibility as compared to 6:4 (MS). 6:4 (MS) contains larger heterogeneity cause by the huge amount of pure Sn phase in the system, while 2:8 (MS) is more homogenous with slight amount of pure Sn. Homogeneity is preferred over heterogeneity as that gives rise to more uniform volume variation.

Figure 44 Peak area of Li_2Sn_5 as a function of voltage for (a) Sn, (b) 2:8 (PM), (c) 6:4 (MS) and (d) 2:8 (MS).

Figure 45 Normalized contribution of Li_2Sn_5 phase to capacity during the 1st two cycles.

6.5 Understanding Alloying of Li with Ge in Melt Spun Sn-Ge

From the work of Linda Y. Lim *et. al.* on the *operando* synchrotron X-ray studies of phase transformation of crystalline Ge, it has been observed and verified by XAS that crystalline Ge underwent an irreversible amorphization process which upon 1st delithiation, remains in amorphous form.¹³¹ The various Li_yGe phases (where $y < 3.75$) are observed to exist in amorphous form from XAS study, except for $\text{Li}_{15}\text{Ge}_4$, which exists in crystalline phase. In this work, the Ge/Ge-rich alloy phase was observed to be absent from XRD spectra from 1st cycle delithiation onwards and the only observed crystalline Li_yGe phase is $\text{Li}_{15}\text{Ge}_4$, which started to form near the end of lithiation at ~ 0.10 V. This is in close agreement with the literature.

Following the EXAFS fitting from Figure 37, the fits below 0.283 V are realized with a 1 Ge-Ge shell and 1 Ge-Li shell and the average Ge-Ge bond distance remains largely unchanged at around 2.45 Å. Examining the local interatomic distances of all known Li-Ge phases, Li_9Ge_4 is the only Li-Ge phase that has a Ge-Ge bond distance similar to that of Ge-Ge bond distance in diamond-cubic Ge. This shows that the amorphous Li-Ge phase that exists together with crystalline Ge (c-Ge) has similar local atomic environment to that of Li_9Ge_4 , i.e. a- Li_9Ge_4 . Hereby, phase with a ‘c’ prefix denotes a crystalline phase while those denoted with an ‘a’ indicates an amorphous phase. Figure 37(b) shows that the coordination number of Ge-Ge decreases rapidly as the voltage approaches the first transformation peak. This is attributed to the phase transformation of the Ge-rich alloy phase/Ge into Li_9Ge_4 , which in the process, breaks up Ge-Ge and Sn-Ge bonds. Due to low backscattering

intensities of the FT, EXAFS fitting could not be carried out satisfactorily for data measured below 0.231 V. However, inferences can be made with reference to Linda Y. Lim *et. al.* work, due to similarities in the differential capacity plots from 0.231 V to end of lithiation.¹³¹ Thereby, the subsequent phase transformations till the end of lithiation can be ascribed as follows. Subsequent lithiation of a-Li₉Ge₄ leads to the formation of a-Li₇Ge₂. Both a-Li₉Ge₄ and a-Li₇Ge₂ coexists, making up the a-Li_yGe phase. c-Li₁₅Ge₄ starts forming at ~ 0.10 V and its amount increases rapidly till near the end of lithiation (Figure 46). The phase fraction evolution of c-Li₁₅Ge₄ during (de)lithiation is calculated from the intensities of the c-Li₁₅Ge₄ (310) peak as described elsewhere.¹⁵¹ At the end of lithiation, a heterogeneous mixture of a-Li_yGe phase and c-Li₁₅Ge₄ phase are observed, as deduced from the ~ 50 % yield of c-Li₁₅Ge₄ phase.

The peak area of c-Li₁₅Ge₄ continues to increase upon delithiation until ~ 0.44 V where it decreases rapidly and finally disappears at 0.538 V (Figure 46). The bond distance and coordination number for Ge-Ge interaction during 1st delithiation are presented in Figure 47 to investigate the phase transformation of the amorphous phases. In the voltage range of 0.503 V to 0.64 V, the Li-Ge structure that is present is likely to resemble that of Li₉Ge₄ since the Ge-Ge bond distance is around 2.45 Å. The absence of Ge-Sn interaction throughout the whole delithiation cycle suggests two possibilities, either (i) there is totally no Ge-Sn interaction present, or (ii) Ge-Sn are present but with coordination number below ~ 0.2 (which is typically the error bar for coordination number parameter in EXAFS fitting) and hence Ge-Sn interaction was not captured in the fittings. After the 2nd phase transformation at 0.617 V, Ge-Li interaction is no longer present, indicating that the amorphous Li_xGe phase resembling a-Li₉Ge₄ has delithiated further to form a-Ge. Interestingly, there appears to be two

distinct Ge-Ge bond lengths in the delithiated amorphous Ge lattice with both having coordination number close to 2 and average bond lengths of 2.45Å and 2.55Å, respectively. The slightly-longer Ge-Ge bond length (~ 2.55 Å) may be due to the presence of strain imposed in the lattice by residual Sn-Ge bonds (undetectable in the EXAFS fitting) when Ge atoms are forming bonds with each other.

Figure 46 Peak area of c-Li₁₅Ge₄ as a function of voltage as determined from Li₁₅Ge₄ (310) peak.

Figure 47 (a) bond distances and (b) coordination numbers for Ge-Ge, Ge-Sn and Ge-Li bonds used in EXAFS fitting for lithiation. The graphs are overlaid on differential capacity plots for comparison purpose. EXAFS fitting on the FTs could not be carried out satisfactorily for data measured below 0.503 V, due to low backscattering intensities of the FT.

To further established the reaction pathway beyond the first cycle and understand the possible contributing factors to reversibility and capacity retention, *operando* XAS measurements were also conducted for the second cycle. The corresponding EXAFS spectra is presented in Figure 48a. As with the first cycle EXAFS spectra in Figure 40b, the first nearest-neighbor shell reduces in intensity as lithiation proceeds, and

recovers partially at the end of the second delithiation cycle. The corresponding EXAFS fitting parameters in Figure 48b & 48c likewise shows no presence of Ge-Li bonds at the end of the second delithiation cycle, as we have observed for the first delithiation cycle in Figure 47a & 47b. Additionally, contrary to the first delithiation cycle, there is only one set of Ge-Ge bonds (~ 2.50 Å) in the second delithiation cycle, implying that there is less strain in the lattice and negligible Ge-Sn bond.

Figure 48 Evolution of Fourier Transform of Ge K edge EXAFS spectra of (a) 2:8 (MS) during 2nd cycle lithiation and delithiation. The red spectrum indicates the delithiation process. (b) bond distances and (c) coordination numbers for Ge-Ge, Ge-Sn and Ge-Li bonds used in EXAFS fitting for 2nd cycle delithiation.

Operando XAS measurements was also conducted for 2:8 (PM) to validate the postulation that Sn atoms are indeed liberated from the Sn-Ge alloy in the melt spun samples and not a byproduct of the interaction of the unreacted pure Sn phase with Ge. From the EXAFS spectra and its corresponding fitting parameters of the first cycle of

2:8 (PM) (Figure 49), the local structure of 2:8 (PM) is observed to closely resemble that of crystalline Ge.¹⁵² As XAS probes the Ge edge only, the results indicate that the physical mixing of pure Sn with pure Ge does not have an effect to the local structure of Ge in the (de)lithiation process. In fact, the β -Sn phase in 2:8 (PM) is observed to follow that of pure Sn electrode materials. This supports and distinct the melt spun samples from the pure Ge phase and physically mixed Sn-Ge sample. This observation attests that the β -Sn produced in-situ is indeed a result of the breaking of Sn-Ge bonds, which leads to the observed reaction pathway. Additionally, the Ge-Li bonds were observed to be present at the end of the first delithiation cycle, which means that simply adding and mixing pure Sn to Ge will not improve the reversibility nor Li storage properties of Sn-Ge type electrode (Figure 25). Similarly, the trend in the second lithiation cycle of 2:8 (PM) (Figure 50) resembles that of the first lithiation cycle and that in crystalline, further supporting the fact that the presence of Sn which is physically-mixed with Ge does not have an effect to the local structure of Ge and is different from the Sn that is produced in-situ from the Ge lattice in 2:8 (MS).¹⁵²

Essentially, the absence of Sn-Ge bonds upon repeated cycling suggests that the Sn-Ge alloy phase structure is metastable and unrecoverable upon 1st delithiation. This is unlike the case of Li alloying type alloy such as SnSb, where SnSb structure is restored by the end of every delithiation and the recovery of the structure promotes better capacity reversibility. This shows the unique reaction pathway of Sn-Ge alloy and its benefits in enhancing Li storage. It is also favorable that no Ge-Li bond is present in the fitting at the end of the delithiation cycle as that shows that the delithiation process in Sn-Ge (MS) is fully reversible, leading to good capacity

retention in subsequent cycles, unlike in the case for Ge, where Ge-Li bonds were found to be still present at the end of the first delithiation cycle.¹³¹

Figure 49 (a) bond distances and (b) coordination numbers for Ge-Ge, Ge-Sn and Ge-Li bonds used in EXAFS fitting for 1st cycle lithiation and (c) & (d) delithiation respectively.

Figure 50 (a) bond distances and (b) coordination numbers for Ge-Ge, Ge-Sn and Ge-Li bonds used in EXAFS fitting for 2nd cycle lithiation

For the crystallite size of pure Ge was found to increase during the second cycle, while no significant changes in crystallite size are observed for the melt spun and physically blended samples (Table 9). However, comparing the normalized capacity contribution for 1st and 2nd lithiation process, there is an increased contribution to capacity during the 2nd lithiation for both MS samples, whereas a decrease was observed for pure Ge and physically blended sample (Figure 51). The increase in capacity provides an indication that there are more Ge atoms available to participate in the Li alloying reaction during the 2nd lithiation. This means that the liberation of Sn atoms from the Sn-Ge alloy lattice is only partially completed during the 1st cycle, and there remain some quantities of Sn atoms in the Sn-Ge alloy lattice that requires further cycling to be fully extracted. Among the 2 MS samples, 2:8 (MS) exhibits a higher 2nd lithiation capacity contribution as compared to 6:4 (MS), which may be the result of more efficient ions and electrons transport.

Table 9 Crystallite size (in nm) of Li₁₅Ge₄ during 1st and 2nd cycles.

Sample	1st Cycle (nm)	2nd Cycle (nm)	Δ (%)
6:4 (MS)	25.21	27.53	+ 9.20
2:8 (MS)	37.52	37.71	- 0.50
2:8 (PM)	45.57	46.42	+ 1.86
Ge	42.80	55.12	+ 28.79

Figure 51 Normalized capacity contribution from $\text{Li}_{15}\text{Ge}_4$ during 1st and 2nd lithiation.

Comparing the crystalline $\text{Li}_{15}\text{Ge}_4$ phase in 2:8 (MS) to the other samples, both MS samples are observed to reversibly form $\leq 50\%$ of c- $\text{Li}_{15}\text{Ge}_4$ upon repeated cycling. As shown in Figure 52, 50% or less of the original Ge were lithiated to c- $\text{Li}_{15}\text{Ge}_4$ phase by the end of lithiation for both MS samples. This deviates from the typical phase transformation mechanism where Li_yGe phases are expected to transform mostly into c- $\text{Li}_{15}\text{Ge}_4$, like those observed in pure Ge and 2:8 (PM) where over 80% are converted into c- $\text{Li}_{15}\text{Ge}_4$. Combining this with the observations from *operando* XAS, it suggests that the MS samples possibly contain a larger fraction of a- Li_yGe phase(s) in the range of $2.25 < y < 4.4$ at the end of lithiation as compared to pure Ge and 2:8 (PM). The presence of a greater amount of highly-lithiated a- Li_yGe phases may help in lessening the volume variation during lithiation/delithiation and thus improve the cyclability of the electrode by sacrificing some capacity. The change in thickness of the electrodes before cycling and after 2 cycles are measured to determine if the critical parameter in defining the exceptional Li^+ storage properties is indeed due to the Sn-Ge alloy phase. The results are presented in Table 10.

Figure 52 Amount of c-Li₁₅Ge₄ as a function of voltage over 2 cycles

Table 10 Thickness of electrodes before and after 2 cycle

Sample	Pressed (μm)	After 2 cycles (μm)	% Δ
Sn	4.0	28.7	617.5
Ge	4.7	12.9	176.8
2:8 (PM)	4.4	16.7	276.1
2:8 (MS)	4.5	7.2	59.3
6:4 (MS)	4.3	21.4	396.5

Pure Sn electrode underwent the largest change in thickness, i.e. 617.5% as compared to the other electrodes. As will be shown in another work elsewhere, the drastic change in thickness in pure Sn can be attributed to the presence of residual Li-Sn phases, which build up over time, upon repeated cycling. Interestingly, 2:8 (MS) undergoes the least change in thickness among the samples investigated, almost ten times lesser than pure Sn and three times lesser than pure Ge. As shown in Figure 44, there are no residual phases of Li₂Sn₅ and LiSn observed for 2:8 (MS) at the end of cycles, whereas

some amount of residual Li_2Sn_5 and LiSn are present in 2:8 (PM) sample. The incomplete removal of Li from the Sn lattice may arise from the sluggish kinetics of Sn and causes pulverization which leads to capacity fading.¹³⁷ Comparing the phases present in the MS samples, it may be postulated that the amount of Sn-Ge alloy phase present plays a critical role in alleviating volume change. It may be suggested that due to the unique reaction pathway of the alloy phase, it impedes the full transformation of a- Li_yGe to c- $\text{Li}_{15}\text{Ge}_4$, and help lessen the degree of volume variation. In this case, the cycling stability is also partially determined by the amount of pure Sn phase in the system. From the collective results from *operando* x-ray studies and thickness change measurement, it may be predicted that the preparation of a pure Sn-Ge alloy phase without unreacted Sn phase will likely leads to more efficient volume variation control.

6.6 Proposed Reaction Mechanism Model for Sn-Ge Alloy

By correlating the analysis from both XRD and XAS, a general reaction mechanism scheme for Sn-Ge prepared via melt spinning can be proposed. Herein, it is proposed that the Sn-Ge materials prepared via MS process deviate from typical stepwise reactions of active/active system. During 1st lithiation in the voltage range of open circuit voltage to 0.4 V, the pure β -Sn phase in the system undergoes stepwise Li alloying reactions, transforming from $\beta\text{-Sn} \rightarrow \text{Li}_2\text{Sn}_5 \rightarrow \text{LiSn} \rightarrow \text{Li}_x\text{Sn}$ (for $x \leq 4.4$), while Ge undergoes ESA from ~ 0.3 V till end of lithiation. It is believed that the concurrent amorphization of Ge helps to ease and buffer the huge volume change of high Li content Li_xSn phases, since the pure Sn resides within the boundaries between Ge-rich phases as observed previously in Figure 19. Just before the occurrence of the

first Li-Ge phase at ~ 0.33 V, Sn-Ge bonds in the Ge-rich alloy phase are broken, liberating Sn atoms *in situ* from the Ge lattice. Given the voltage at which β -Sn was liberated in-situ (~ 0.3 V), the β -Sn species has to compete with α -Ge, Li_xSn and Li_yGe phases concurrently for Li ions during lithiation. This may result in some unlithiated species or “unlithiated core – lithiated shell” configuration among the species. Presence of these species provide additional point electrical contacts for efficient electrons transport and also act as buffer for volume change by relieving stress/strain in the system, e.g. they are inert/undergo very little change till end of lithiation. These species will take part in lithiation in subsequent cycles. This is analogous to capsule medicine, where the drugs take time to be fully released/reacts.

In this context, such mechanism is found to be beneficial in the overall Li^+ storage properties and provide another means to design electrode materials for anode. As this is the first ever occurrence and observation of such reaction pathway for lithium ion batteries, it will be termed, the “*timed release capsule model*”. After the liberation of Sn from Sn-Ge alloy, the “freed” Ge alloyed with Li to form amorphous Li_9Ge_4 , which coexist with α -Ge and occurs around 0.33 V. While there is no evidence of other amorphous Li-Ge phases after the first lithiation peak, due to low backscattering and k space signals, it can be generalized that the subsequent lithiation of amorphous Li_9Ge_4 forms amorphous Li_yGe as reported in the literature which further lithiates to form crystalline $\text{Li}_{15}\text{Ge}_4$ at 0.10 V.¹³¹

During delithiation, the removal of Li^+ from crystalline $\text{Li}_{15}\text{Ge}_4$ forms amorphous Li_9Ge_4 and eventually amorphous Ge, while the Li_xSn phases delithiate into crystalline

β -Sn. On further cycling, the “capsules” containing Sn-Ge alloy/unlithiated species will continue to release unlithiated species to participate in lithiation until all capsules are depleted. A generalized “*timed release capsule model*” for Sn-Ge during the 1st and 2nd cycle are depicted in Figure 53 and 54 respectively. Preparation of such alloy systems can likely be generalized to include any rapid solidification techniques with appropriate cooling rates that can extend the solubility limits. However, future works need to be done to ascertain the abovementioned postulation.

Figure 53 Timed release capsule model - during 1st cycle.

Figure 54 Timed release capsule model - during 2nd cycle.

6.7 Conclusions: Understanding reaction mechanism of melt spun Sn-Ge

From the time resolved *operando* XRD and XAS studies, it has been observed that the Sn-Ge alloy phase behavior deviates greatly from other Sn alloys such as SnSb, whereby structural reversibility is observed upon delithiation for SnSb alloy. Instead, the pure β -Sn phase in Sn-Ge (MS) was found to first undergo stepwise Li-Sn alloying reactions from open circuit voltage (OCV) to ~ 0.4 V. After which, just before the occurrence of the first Li-Ge alloying reaction, Sn atoms are liberated *in-situ* from the Sn-Ge alloy phase, with Ge concurrently undergoing ESA. Since Sn atoms are liberated at a potential where other species present in the electrode are already lithiating, the newly liberated β -Sn will have to compete with them for Li ions. This may results in some incompletely lithiated/unlithiated species. Such species are believed to be beneficial by not only buffering volume expansion (since they are temporarily inert/minimum volume expansion) but also provide electronic pathway to facilitate electrons transport. This is the first observation of such reaction mechanism for alloying-type materials and will be called “timed release capsule” model, as it is analogous to how capsule medicine are released. The approach demonstrated in this work establishes a new means to the design of electrode for anode materials.

Chapter 7 Conclusions and Future Works

7.1 Conclusions

The search for suitable electrode materials for lithium-ion batteries is among the key technological challenges for the advancement of battery technologies and emerging applications. For anode materials, high capacity, low working potential, good reversibility and fast charge/discharge are some of the key criteria. Current approaches adopted generally involved the synthesis of nano-sized structures with various morphologies and choosing materials that either undergo lithium alloying or lithium conversion reaction because of their higher theoretical capacities. In this work, novel Sn-Ge alloys are fabricated via melt spinning processing, a rapid solidification technique that results in unique microstructures as well as extension of solubility limit in the otherwise almost immiscible mixture of Sn-Ge. This work detailed the methods used in the phase-structure characterization of novel Sn-Ge alloys. After which, the Li storage properties of Sn-Ge (MS) were compared and evaluated against reference samples. Finally, *operando* synchrotron X-ray methods such as XRD and XAS are utilized to elucidate reaction mechanisms of Sn-Ge (MS), from which, a new mechanistic model is proposed.

The key findings that have resulted from this work are summarized as follows:

1. Melt spinning process can extend the solid solubility limits of immiscible systems. In this work, the solid solubility limit of Sn in Ge was determined to be extended from < 1 at. % as documented in the phase diagram of Sn-Ge to 7 - 11 at. %, depending on the concentration of Sn in the starting precursor. Generally, having more Sn in the starting precursor results in the formation of Sn-Ge alloy with higher Sn concentration, but at the same time, also results in a much larger amount of residual pure Sn phase in the Sn-Ge (MS) sample. Starting precursor ratio of Sn: Ge at 2:8 and 1:9 were found to result in the least amount of residual pure Sn phase in the system.
2. Li storage properties of Sn-Ge (MS) samples are strongly dependent on phase composition. Higher concentration of pure β -Sn phase in the sample is detrimental for long term cycling stability as not only will it lead to faster capacity fading but also impede the rate capability. On the other hand, having a large amount of Sn-Ge alloy phase (~ 80 % and above) in the system results in good cyclability that exceeded that of pure Ge and physically blended mixture with the same Sn/Ge ratio cycled at the same current and over the same number of cycles. High and stable capacities of over 1000 mAhg^{-1} (1591 mAhcm^{-3}) were maintained over 60 cycles at a C-rate of 0.1C. Fast rate capability was also observed, with capacities close to 1000 mAhg^{-1} , at C-rates up to 0.5C. Notably, capacity of 500 mAhg^{-1} (795 mAhcm^{-3}) can still be attained at a high rate of 5C. Apart from the extension of solid solubility and

unique microstructure that resulted from MS process, keeping particle size at $\sim < 10\ \mu\text{m}$ also results in high volumetric capacity which is among the highest reported to date for anode materials is also realized.

3. Reaction mechanism of Sn-Ge (MS) is found to deviate from the typical stepwise lithium alloying reaction through *ex-situ* X-ray studies conducted at various cut-off voltages during 1st cycle lithiation/delithiation. Sn-Ge alloy is found to undergo a precipitation-alloying reaction, where Sn in the Sn-Ge alloy is observed to precipitate out *in-situ* to form β -Sn nanograins, while simultaneously, Ge transforms from crystalline to amorphous state. The crystalline to amorphous transformation of Ge is irreversible, and results in an amorphous matrix of Ge with nano-sized crystalline β -Sn embedded in it upon further cycling.
4. Time resolved *operando* synchrotron X-ray studies provide insights into the real time phase transformation/formation of melt spun Sn-Ge during lithiation/delithiation. The pure β -Sn phase in Sn-Ge (MS) is the first species to undergo stepwise Li-Sn alloying reactions from OCV to $\sim 0.4\ \text{V}$. After which, just before the occurrence of the first Li-Ge alloying reaction at $\sim 0.3\ \text{V}$, Sn atoms are liberated *in-situ* from the Sn-Ge alloy phase, as observed by the disappearance of Sn-Ge interactions from EXAFS fitting. Concurrently, Ge undergoes ESA. Thereafter, the Li-Ge alloying reactions take place. The Ge phase in Sn-Ge (MS) is found to have much better reversibility of 76.2% recovery as compared to 27.6% for pure Ge.

Since Sn atoms are liberated much later as other lithiation reactions are in progress, it has to compete with other existing species for Li ions. This may then results in unlithiated species/incomplete lithiation which then act as buffers till the end of lithiation and provide point electrical contacts for the efficient transport of electrons.

5. A mechanistic model for melt spun Sn-Ge is proposed. The liberation of Sn *in-situ* from the Sn-Ge alloy is a new phenomenon that has previously not been observed and documented. Based on the reaction sequence, a “timed release capsule model” is proposed, suggesting that the reaction mechanism of melt spun is akin to that of timed drug delivery capsule medicine. The liberation of Sn atoms from Sn-Ge alloy is timed and occurs only during lithiation. Given the voltage at which it is released, it has to compete with other existing species for Li ions, resulting in unlithiated species/incomplete lithiation. Such species aids the buffering of volume expansion and also helps relieve the stress/strain in the system, before taking part during the next lithiation. This unique reaction pathway that has been discovered in this work is shown to be beneficial in containing volume expansion as well as enhancing the overall Li storage properties. The approach demonstrated in this work establishes a new strategy to the design of electrode for anode materials.

7.2 Future Work I: Further Understanding of Proposed Model

Due to time constraint, this work is not able to cover all aspects of the reaction mechanism. As several Li_yGe phases as well as Li-rich Li_xSn phases exist in amorphous form, their kinetics and reversibility need to be examined. In particular, following the real time phase transformations for at least 2 full lithiation/delithiation cycles via synchrotron XAS, at both Ge and Sn edges are required. Adding on the capability of *in-situ* TEM observations, will allow both quantitative and qualitative analysis of the reaction mechanism. Apart from mechanistic understanding of the proposed model, modeling and simulations will allow us to gain insights into the kinetic aspects.

In addition to phase/structure characterizations, electrochemical characterizations such as AC impedance analysis needs to be carried out during (de)lithiation and over several cycles to determine the differences in resistances of various charge-transfer steps. The 2:8 (MS) samples needs to be compared against 2:8 (PM), pure Sn and pure Ge to discriminate the possible enhancing mechanisms between the Sn-Ge alloy from the pure elements. From which, combined with the current understanding on the reaction pathway and phase transformation mechanism, a more holistic picture can be painted.

7.3 Future Work II: Generalization of the Proposed Model

In this work, only Sn-Ge was investigated. Getting a pure Sn-Ge phase, without any residual pure Sn phase will help in determining the optimum Sn-Ge alloy composition that will result in the best Li storage properties. There is also the need to validate if other rapid solidification techniques can be used to prepare such alloys such that the process can be generalized. Apart from the materials aspect, the proposed model need to be validated by preparing analogous systems and determine if it can be generalized and applied in other systems as well, following certain prerequisites.

Based on the knowledge gained from this work, the following are some key criteria in selecting the right materials system:

1. The two elements are almost immiscible in the phase diagram
2. One of the elements undergo ESA upon lithiation
3. Both elements are electrochemically active towards Li
4. Elements with good electrical conductivities

With that in mind, systems with general formula of M-N (where M = Si, Ge and N = any Li-alloying element) will be suitable candidates. The closest analog to Sn-Ge will be Si-Sn. Another attractive candidate to explore will be Al-Ge. Compared to other Li-alloying elements, Al only undergoes a single phase transformation, i.e. from Al to LiAl at room temperature, from previous works in the literature.^{153, 154} LiAl has a theoretical capacity of 993 mAhg⁻¹ which is comparable to Sn. It is worth mentioning that the volume expansion for Li-Al alloying is 97%, which is at least three times

smaller than that of Group 14 elements and with only a single phase transformation, should result in even better cycling stability.

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Appendix A: Supporting Information

Figure A1 Micrographs showing the particle size of (a) Sn-Ge (MS), (b) pure Sn and (c) pure Ge precursors. Reproduced by permission of The Royal Society of Chemistry.¹⁰³

Figure A2 A typical Rietveld refinement fitting

		N	R (Å)	σ^2 (10^{-3} Å ²)
First shell	Ge-Ge	3.67(8)	2.453 (3)	3.7 (2)
	Ge-Sn	0.33(8)	2.624 (35)	7.5 (20)
Second shell	Ge-Ge	11.02(24)	4.026 (9)	13.5 (11)
	Ge-Sn	0.98 (24)	4.385 (20)	3.3 (19)
Third shell	Ge-Ge-Sn	11.02 (24)	4.733 (12)	11.0 (2)
		0.98 (24)	4.749 (28)	12.5 (30)

Table A1 Summary of single-scattering paths used in the fit, and local structure parameters based on quantitative analysis of Fourier transforms of k^2 -weighted EXAFS spectra for Sn-Ge (MS). The alloy model used in the fitting involves having 25% of Ge in diamond-cubic Ge replaced with Sn. For example, in the first coordination shell, one of the four Ge atoms is replaced by a Sn atom. Uncertainties in the last digit(s) are given in parentheses. The percentage of Ge is refined to be $91.8\% \pm 2\%$. The first, second and third shell Ge-Ge bond distances in diamond cubic Ge are 2.449 Å, 3.999 Å, and 4.690 Å respectively. Reproduced by permission of The Royal Society of Chemistry.¹⁰³

Figure A3 Cyclic voltammetry profiles of 2:8 (MS) at various scan rates.

Figure A4 Typical operando XRD spectra from 1st and 2nd cycle.