Synthesis and electrochemical performance of aluminum antimonide alloy anode prepared by melt spinning

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NANYANG
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**SYNTHESIS AND ELECTROCHEMICAL PERFORMANCE
OF ALUMINUM ANTIMONIDE ALLOY ANODE
PREPARED BY MELT SPINNING**

DANIEL JULIAN KHARISTAL

**SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2014**

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University

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Abstract

In this work we have successfully synthesized melt spun Al-Sb alloy and studied the electrochemical performance of these Al-Sb alloy as anodes for lithium ion batteries. The melt spun Al-Sb alloy has unique morphological structure compared to the conventional cast Al-Sb alloy. In high Al content the AlSb phase is surrounded by Al matrix while in high Sb content the AlSb acts as a matrix and surround the Sb phase. The size of the AlSb phase ranged from 0.1 to 1 μm , which is much smaller compared to the conventional cast Al-Sb alloy. Another advantage in using melt spinning process is that it can produce materials with high throughput and high purity metal alloy products with little to no impurities, which is beneficial to the battery performance.

The melt spun Al-Sb alloy exhibited improved electrochemical performance with the first discharge capacity of 635 mAh/g, high Coulombic efficiency of 85%, and good cycling performance of 504 mAh/g after 80 cycles is exhibited by Al₄₀Sb₆₀ samples. A good electrochemical performance is also demonstrated by the Al₅₀Sb₅₀ samples with first discharge capacity of 600 mAh/g and after 80 cycles was able to maintain good capacity of around 470 mAh/g.

We propose that the battery performance of the melt spun Al-Sb alloy is mainly influenced by the amount of AlSb phase in the structure and the ability of AlSb phase to reform itself after cycling. The ability of the AlSb phase to restructure and reform itself after reaction with lithium (dealloying) is crucial in order to maintain good battery performance and cycleability of the anodes. The Al₆₀Sb₄₀ and the Al₅₀Sb₅₀ demonstrated

good battery performance due to the most of AlSb phase able to maintain structural integrity and not breakdown into individual Al and Sb phase upon cycling, as evidenced by the post mortem XRD characterization showing high amount of AlSb phase after lithiated for 100 cycles, while the Al₈₀Sb₂₀ and Al₂₀Sb₈₀ exhibited poor performance due to the large amount of inherent Al and Sb phase in the structure and the breakdown of some of the AlSb phase into individual Al and Sb particles. The breakdown of AlSb phase into individual Al and Sb particles has led to cracking and loss of electrode contact due to the large volume expansion created by Al and Sb phase reaction with lithium during cycling process.

The discussed findings highlights the advantages of the melt spun Al-Sb alloys as anode and the possibilities for further development of this material as a potential candidate for the next generation of anode material for lithium ion batteries with superior electrochemical properties.

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Chapter 1

Thesis Scope and Objectives

1.1. Thesis scope and motivation

The demand for high performance and efficient energy storage devices for powering modern electronic devices has been steadily increasing in the past few years. The drive for renewable energy sources for power generator and low cost green electric vehicles also contributing to the demand of efficient energy storage devices. Lithium ion battery is one of the most important energy storage devices available today. Unfortunately, the current battery technology can barely keep up with the demand of modern electronic equipment due to their low capacity, poor cycle life, slow charge / discharge rates, and high cost of electrode materials. Therefore, development of facile, low cost, and environmental friendly approaches have attracted considerable interest in the scientific and engineering communities.

Anode material has been researched with considerable interest from the scientific community due to graphite as the current commercial anode material has so far failed to meet the expectations and demands of high performance battery system. Metallic alloy such as Al, Sb, Si, and Sn has been identified to have great potential to replace graphite as anode material due to the high theoretical capacity of these materials⁹⁻¹².

Fabrication of intermetallic compounds (A_xB_y) that have a strong structural relationship with their lithiated products have been pursued to reduce the detrimental effect of volume

expansion resulting from the lithium insertion / extraction of these metallic alloys¹³⁻¹⁵. Large volume expansion can result in a structural collapse of the electrode and contact loss of the active materials from current collector, leading to low capacity and rapid capacity fade during cycling, especially at high current densities.

Al-Sb alloy is one of anode materials that have a great potential due to the low cost, environmentally friendly, and have a high theoretical capacity (LiAl 993 mAh/g and Li₃Sb 660 mAh/g). Al-Sb alloy is a zinc – blende type structure that provides a three dimensional interstitial space for lithium insertion^{50,51,53}. Lithium can be inserted in the open framework structure of the Al-Sb alloy followed by Sb extraction. Furthermore, due to the reaction potential difference, the reaction with lithium will be done in a stepwise manner. Lithium ions will be inserted into the more reactive Sb first while the unreacted ductile Al will acts as a buffer matrix, thus reducing the volume expansion. Although Al-Sb has great potential as anode material, until now there is little interest in developing this material due to the irreversible capacity and rapid capacity loss demonstrated in the Al-Sb bulk alloy materials. We believe that the full potential of Al – Sb as replacement anode for lithium ion batteries has not been achieved, and by employing particle size control, the electrochemical performance of this material can be further improved.

Nanostructuring can significantly enhance the electrochemical performance of electrode materials for lithium ion batteries. By reducing the size of the particle to nanosize, the lithium diffusion length is considerably shortened, thus making the lithium insertion / extraction to the structure faster and easier without considerable damage to the structure³⁶⁻³⁸. Furthermore, the high density of the grain boundaries in nanocomposites provides a fast diffusion path for lithium ion and also acts as additional Li ion sites³⁹⁻⁴⁰.

Melt spinning is a rapid solidification process with a rapid cooling rate of 10^6 K / resulting in materials with nanocrystalline or amorphous metallic phase features with unique material properties. The advantage in using this technique is that melt spinning is a high throughput and high scalability process, which can produce a large quantity of high purity materials, making this process feasible and scalable for industrial application. Furthermore, compared to other various chemical synthesis methods used to prepare alloy composites, melt spinning can deliver high purity metal alloy products with little to no impurities. Numerous reports have indicated that the use of melt spinning results in material with unique nanocrystalline properties which have improved electrochemical performance compared to conventional bulk materials. In this thesis, we investigate the synthesis of Al–Sb alloy and the electrochemical performance of this alloy for use in lithium ion batteries, as to the best of our knowledge, the use of Al–Sb alloy fabricated by melt spinning as anode material has not been investigated.

1.2. Objectives

- a. To synthesize Al–Sb alloy using melt spinning technique and study the effects of different Al and Sb composition on the morphological properties of Al – Sb alloy.
- b. To study the electrochemical performance of the Al – Sb alloy synthesized by melt spinning as anode material for lithium ion battery.

Chapter 2

Literature Review

2.1. The Energy Storage Challenge

In recent years, climate change and the imminent depletion of fossil fuels drive the need to replace current petroleum based energy sources with an environmentally clean and renewable energy sources to alleviate the world's energy demand. Solar and wind power have potential as one of the renewable energy sources, and Electric Vehicles (EV) and Hybrid Electric Vehicles (HEV) has become increasingly popular for transport vehicles. Also, advances in electronic devices technology requires an ever increasing demand of higher performance energy storage technology to power these devices. Thus, the development of high performance energy storage devices is of high importance and is one of the hottest research topics in the science and technology community.

Lithium ion batteries is one energy storage system that has been considered as the system of choice for powering electronic devices and electric vehicles due to its high energy density, efficiency and long cycle life. Lithium ion batteries are light, compact, and with a voltage range of 4V and a specific energy ranging between 100Wh/kg and 150Wh/kg¹.

Among the existing battery technologies, Li ion batteries currently outperform other systems and are dominating sales for the energy storage industry, as shown in Figure 1.1, due to the high energy density, lightweight, and design flexibility². This explains why Li ion batteries are receiving the most attention from researchers at both fundamental and applied levels.

Figure 1.1 Li-ion battery market demand due to mobile IT devices².

In a conventional system, a lithium ion battery typically contains a graphite anode, a cathode of lithium metal oxide (e.g. LiCoO_2 , LiMnO_2) and an electrolyte containing a solution of lithium salt (e.g. LiPF_6) in a mixed organic solvent (e.g. ethylene carbonate – dimethyl carbonate, EC–DMC) embedded in a separator felt. Figure 1.2 shows the common Li ion battery configuration. Upon charging, the Li ions migrate from the cathode (deintercalation) through the electrolyte to the anode while the electrons transfer from the cathode to the anode through an external electric field. During discharge process, the opposite happens. The chemical reactions on anode and cathode can be described as follows³ :

In this formula, the LiMO_2 is the cathode materials and the C is a carbon anode materials.

Figure 1.2 Schematics of a common Li ion battery¹.

Due to the increasingly advanced and high performance electric devices, there are higher demands for battery with larger energy density, higher power, and longer cycle life than those currently available. The electrochemical properties of electrode materials determine the specific capacity and the output voltage, which contribute to the energy density of battery. Thus, to increase the performance of lithium ion battery the properties of the anode and cathode materials must be improved.

The performance of the battery system, for example the cell potential, capacity, or energy density is related to the intrinsic properties of the materials that are used in the positive and negative electrodes. The cycle-life and lifetime of the battery are dependent on the nature of the interfaces between the electrode and electrolyte, while the safety is a function of the stability of the electrode materials and interfaces. The selective use of

materials for use in the negative and positive electrodes, and the right electrolyte combination can minimize unwanted reactions between the electrode and electrolyte, thus achieving the best performance of electrode and electrolyte⁴.

In the negative electrode, or anode carbon based materials are frequently used for the production of commercially available lithium ion batteries. The Li-interacted carbons show a low potential close to the Li metal anode, however it is safer and more reliable than the Li metal anode, as the dendrite formation in the Li metal which can lead to explosion and electrode failure can be avoided. Graphite is one of the carbonaceous materials that are widely used for anode materials due to the stable specific capacity of around 372 mAh/g, small irreversible capacity, and good cycling performance. Although graphite has been a success commercially, it is known that carbonaceous material such as graphite suffer from solvent co-intercalations in propylene carbonate based electrolytes which can results in interlayer expansion and degradation of the graphite structural integrity. The gravimetric and volume capacities of graphite are also rather limited and it is not enough to satisfy the high demand of supplying power for modern electronic devices⁵. In order to achieve a higher performance battery, a dedicated research and exploration of new materials with high capacity, high energy density and electrochemical stability is of utmost importance.

2.2. Selection of Anode materials for Li ion batteries

There are different types of anode materials. Usually the materials are differentiated by the type of reactions with the Li ion. There are three types of reactions that occurred during

lithiation, which are insertion reaction, alloying reaction, and conversion reaction⁶, as shown in Figure 1.3. Metallic and semi metallic materials such as Al, Si undergo alloying reaction with Li, while transition metal compounds M_aX_b undergo conversion reaction during lithiation resulting in metallic particles embedded in a matrix of Li_yX^6 .

Figure 1.3. A schematic representation of the different reaction mechanisms observed in electrode materials for lithium batteries. Black circles: voids in the crystal structure, blue circles: metal, yellow circles: lithium⁶.

Alloy metals have been shown to be capable of reversibly react with large amount of Li to undergo alloying reaction upon polarization to form Li_xM alloys that yield high specific capacities (with x up to 4.4)⁷. These types of materials have the highest gravimetric and volumetric capacities among the possible potential candidates. However, due to the

large amount of lithium uptake that occurred during lithiation process, a huge volume expansion in the structure will be resulted. The comparison of several metallic materials capacity and volume expansion is presented in Table 1.1. Alloy anodes have significantly higher theoretical specific capacities compared to the commercially available graphite anodes. Even with the full volume expansion of lithiated products taken into consideration, the charge densities of the alloy anodes are still far superior to those of commercial graphite.

Table 1

Comparison of the theoretical specific capacity, charge density, volume change and onset potential of various anode materials.

Materials	Li	C	Li ₄ Ti ₅ O ₁₂	Si	Sn	Sb	Al	Mg	Bi
Density (g cm ⁻³)	0.53	2.25	3.5	2.33	7.29	6.7	2.7	1.3	9.78
Lithiated phase	Li	LiC ₆	Li ₇ Ti ₅ O ₁₂	Li _{4.4} Si	Li _{4.4} Sn	Li ₃ Sb	LiAl	Li ₃ Mg	Li ₃ Bi
Theoretical specific capacity (mAh g ⁻¹)	3862	372	175	4200	994	660	993	3350	385
Theoretical charge density (mAh cm ⁻³)	2047	837	613	9786	7246	4422	2681	4355	3765
Volume change (%)	100	12	1	320	260	200	96	100	215
Potential vs. Li (~V)	0	0.05	1.6	0.4	0.6	0.9	0.3	0.1	0.8

Table 1.1 Comparison of Specific capacity of several electrochemically active metal elements⁸.

Another advantage of the alloy anodes is their slightly higher operation potential against lithium compared to graphite. For example, both Si and Al anodes have an onset voltage potential of 0.3 – 0.4 V above Li/Li⁺. This potential averts lithium deposition on the electrode which could cause safety concerns, as happened with the graphite anodes with 0.05 V vs. Li, while also avoiding the energy penalty of battery cells that is assembled with LTO anodes which have potential of 1.5 V vs. Li⁸.

The main challenge of using these alloy anodes for battery materials is the large volume change during lithium insertion and extraction due to the high amount of lithium uptake, that leads to degradation of the active materials and poor cycle stability^{9,10}. Early studies⁹⁻

¹¹ found out that most of the alloy anodes had high initial irreversible capacity (the difference between charge and discharge capacity) and huge capacity fade during cycling. Figure 1.4 shows the charge / discharge curves of a silicon alloy anodes¹¹. From the charge / discharge profile, it is apparent that the charge capacity (alloying reaction) is much higher compared to the discharge capacity (dealloying reaction) in the first cycle. Furthermore, during the next few cycles, the capacity decreases dramatically compared to the first cycle. Other alloy systems, such as Sb⁹, Sn¹⁰, and Al¹², have also demonstrated similar behavior.

Figure 1.4. Charge – discharge profiles of a pure silicon anode with an average size of $10\mu\text{m}^{11}$.

There are several factors that are considered to be the cause of the rapid capacity fade and irreversible capacity during cycling. The first factor is the loss of contact between the electrode and the current collector. Due to the large volume change occurred during cycling, cracking and breakdown of the active materials will lead to contact loss with the current collector or the conductive carbon. This breakdown of conductive network is demonstrated by a significant increase in the internal resistance of an AlSi anode at 0.4 V during the

lithium extraction process, as shown in Figure 1.5 below. Due to the rising resistance and the isolation of the Si particles, some lithium will not be fully extracted from the structure and remained inside. As a consequence of the incomplete lithium extraction, rapid capacity fade began to occur with increasing cycle number. The large volume change occurred during lithiation puts the Si particles and the surrounding matrix under compressive stresses and thus remained mostly intact. Meanwhile, when delithiation process occurs, the contractions of the Si particles result in large tensile stress that could eventually lead to the cracking of the active materials and the entire electrode. An AFM study has also confirmed that the cracking mostly occurred during the delithiation process¹⁴.

The formation of a solid – electrolyte interface (SEI) films also plays a role in the capacity fading of the alloy anodes. The SEI formation usually involves the decomposition of the electrolyte that is composed of solvents and salt. This decomposition occurs in a potential range of 0.4 – 0.9 vs. Li^+/Li causing irreversible capacity loss due to the loss of lithium ion. Some studies using HRTEM, FTIR, and XPS have confirmed the presence of the passivating SEI films on alloy surfaces due to the reaction of lithium with the electrolyte at the alloy anodes surface¹⁵⁻¹⁸. The SEI film is composed of mainly Li_2CO_3 , various lithium alkyl carbonates (ROCO_2Li), LiF , Li_2O and non-conductive polymers.

Figure 1.5. The potential and capacity frequency for the kinetic (f_k^*) and intrinsic impedance (f_{i1}^*) as a function of initial Li insertion capacity for an AlSi electrode containing 8 wt.% carbon, and 10 wt.% PVDF. f_{i1}^* is the characteristic frequency for the first semicircle of the intrinsic impedance¹³.

The formation of SEI on alloy anodes is reported to be different than the formation in graphite anodes. The formation of SEI film on alloy anodes is observed to be a continuous

process of breaking off and reforming due to the repeated volume changes that occur during cycling^{15, 16}. Furthermore, with increasing cycle number, an increasingly thick SEI films on the electrode surface and higher amount of electrolyte salt side reaction products has been observed.

Although lithium insertion / extraction is mostly a reversible process, some of the lithium ions might be trapped permanently inside the structure due to the slow lithium release kinetics, formation of highly stable lithiated compounds, and strong bonding with less coordinated atoms at defect sites¹⁹⁻²¹. Due to the huge volume change and a transformation of structured occurred during lithium insertion/ extraction, Li can be trapped permanently at the defect sites that are present at the surface, interface, or grain boundaries of the alloy anodes. Furthermore, the presence of impurities in the alloys such as carbon, oxygen, phosphor, or sulfur could lead to the formation of a stable lithium compounds, and reducing the capacity of the electrode material²².

Metallic materials are known to be reactive with oxygen and water, and as a result an oxide layer is usually formed on metal surfaces if the preparation is not done carefully. Lithium reacts with oxygen to form Li_2O at 0.8-1.6 V potential, and due to the low atomic weight of oxygen, even a low amount of oxide in the structure could lead to capacity fading²³. One last factor that affects the irreversible capacity loss in the alloy anodes is the aggregation of alloy particles. The volume expansion of the anodes can lead to a high pressure mounting on the alloy particles itself and causing a welding effect and eventually particle aggregation. This agglomeration of particles is unwanted, as it can lead to an increase in Li diffusion length and the presence of the SEI films inside the agglomerated particles²⁴.

2.3. Approaches in the development of advanced alloy anodes

In order to minimize the rapid capacity fading and huge irreversible capacity, numerous approaches have been proposed and explored to alleviate the negative effect of the volume variation that the alloy anodes experienced during lithiation. The approaches are as follows:

(A) Multiphase composites

One of the most interesting and feasible approach to improve the electrochemical performance is to utilize a combination of compound, or multiphase composites instead of a single metal. By using this approach, the active alloy particles can be dispersed within a composite matrix so that the host matrix can absorb the volume change of the active particles, and thus maintaining structural integrity of the electrode and the stability of the electrode material²⁵. The host matrix can minimize the aggregation of the particles during lithium insertion / extraction by acting as a spacer between the alloy particles²⁶. There are 3 types of composite phases of host matrix which are: (i) inactive host matrix, (ii) active host matrix, and (iii) carbon host matrix.

For inactive host matrix composites, it composed of active metal material and an matrix material that is electrochemically inert, such as Fe, Cu, or Nb^{27,28}; an oxide such as Al₂O₃²⁹; ceramic such as SiC³⁰, or an alloy such as FeSi₂³¹. The buffering effect of the inert matrix has been observed by SEM examination of a cycled Al anode, which demonstrated no visible cracks in an Al/SiC electrode, while the pure Al metal has severe cracking in the first cycle³⁰. A crucial requirement for the selection of inactive matrix host is that the material must have high ionic and electronic conductivity, so that the matrix does not inhibit the lithium diffusion or ion transfer from the active particles that can lower the overall capacity of the electrode. The matrix must possess low elastic modulus, low ductility, and

high strength in order to keep the active materials in highly compressive stress during lithium insertion to limit volume expansion and reduce electrode cracking³².

The second multiphase composite is the active host matrix. In this anode, both the active materials and the host matrix could react with lithium. The advantage of using this composite is that one component can be lithiated first while another component can buffer against volume change due to the difference in onset potential between the two materials. One example of this composite type is SnSb alloy, in which Sb is the more active phase that reacts with lithium at ~ 0.9 V vs. Li/Li^+ , while the Sn phase with potential of 0.6 V has yet reacted with Li, and thus can act as a buffer against volume expansion of lithiated Sb phase³³.

The third multiphase composite is the carbon based composites. Studies have reported the advantage of using carbon coating to increase the performance of alloy anodes³⁴⁻³⁶. The increased performance is due to the improved electronic conductivity, good ionic conductivity, low volume expansion, lithium storage ability and tolerance to mechanical stress^{34,35}. Figure 1.6 shows the improvement in capacity retention of a Sb anode by adding carbon (C) and graphite (G). It has been observed that the addition of carbon coating can minimize SEI layer formation and limit the cracking and pulverization of particles by applying compressive stress on the alloys.

Figure 1.6. Cycle performance comparison for Sb/carbon/graphite, Sb/carbon and Sb composites cycled under different voltage windows³⁴.

(B) Particle size control

Nanostructuring has been widely accepted as a crucial and effective route to enhance the electrochemical properties of the electrode materials. By reducing the particle size to nanoscale range (< 100 nm), the cycling performance can be dramatically improved³⁶⁻³⁸. The improved cycling performance is attributed to the ability of the nanosized materials to absorb large stress and strain without breaking down, as the motion and propagation of the stress dislocations are constrained in the nano grains and particles³⁹. Furthermore, the small size of the particles decreases the lithium diffusion length and electron transfer, and also minimizes the stress created by Li diffusion that is inhomogeneous. The grain boundaries

with high densities could provide a fast lithium ion diffusion path and also acts as extra Li ion sites⁴⁰. The large surface area of the nanoscale also increases the contact area with the electrolyte, and thus allowing a more efficient reaction at the interface between the electrode and electrolyte. However, careful consideration must be done when designing the nanostructure anodes as it is possible for the nanoparticles to have a side reaction with the electrolyte and formation of SEI, which can lead to capacity fading and poor cycle life.

(C) Intermetallics

Thackeray et al^{18,27,41} has proposed and intensively investigated the concept of intermetallic anodes. The concept of intermetallic anodes is to produce lithium host structure that can maintain their integrity and a limited volume expansion during lithium insertion / extraction process. In this structure, the insertion of lithium into the host lattice took place by extracting the other component out and replacing it in the structure. In a Cu_2Sb anode, the lithium insert into the Cu_2Sb structure by extraction of Cu out from the structure to form Li_3Sb while maintaining the integrity of the fcc host Sb sublattice⁴². The structural similarity, fast kinetics, and low volume variation due to the lithium insertion / extraction process provide the good cycling stability of the intermetallic anodes. Cu_6Sn_5 ⁴³ and InSb ⁴⁴ have been investigated as lithium ion battery anodes and have shown good cycling stability over repeated cycling.

(D) Operating Voltage Control

It has been observed that alloy anodes demonstrated improved cycle life when they are cycled within a restricted voltage range instead of a full voltage range³⁴. By reducing the upper or lower voltage potential, the structural integrity of the alloy anodes can be maintained and volume variation minimized. Park *et al*³⁴ reported that by reducing the potential range to 0.8 -2 V the cycling performance of a Sb/C composite improved significantly. However, the drawback in using this method is the reduction of anode capacity. Due to the shorter voltage range potential applied to the alloy anode, less lithium ion are stored inside the structure, thus reducing the anode capacity.

2.4. Lithium reactions in alloy anodes

Generally, there are two groups and three types of alloying reaction with lithium. The first group is an addition reaction and insertion reaction, while in the second group is a displacement reaction⁴⁵. In the first group, lithium ions are inserted to the reactant structure without replacing or extracting components from the reactant. The lithium insertion reaction with the reactant can be described using the following formula:

The reactant M is an element or a compound. Depending on whether a phase transformation takes place, the reaction can be divided into solid solution reaction and addition reaction⁴⁵. In solid solution reaction, when lithium insert into the framework structure there is no change in phase or structure occurred. In the addition reaction, there is a change in phase structure as the lithiated phase of Li_xM is different compared to the parent phase M, in other words the lithium insertion reaction induces a structural change from M

to LiM_x ⁴⁶. In elements such as Si, Sn, Al, and Sb, due to the low solubility of lithium the lithium insertion / extraction process are considered as addition reaction. Mg and amorphous Si are examples of solid solution reactions.

According to the Gibbs phase rule, the amount of degrees of freedom f in a closed system at equilibrium is given by $f = C - P$, where C is the number of the independent component and P is the number of phases that exist in the system under constant pressure and temperature⁴⁷. In a binary system of Li-M where only 1 phase exists, $C = 2$ and $P = 1$; the voltage profile exhibits a sloping (round) shape where the electric potential of the reaction is a degree of freedom and varies with the lithium concentration. Meanwhile for a two phase addition reaction, in a binary system the degree of freedom is zero, therefore the electrode potential under equilibrium conditions is independent of the overall composition. On the voltage profile for the two-phase equilibrium region a constant plateau can be observed.

In a displacement reaction, one component M of an alloy compound MN_y will react with lithium ions while another component N is replaced or extracted from the structure⁴⁸. The extracted element N could react or is inert towards lithium. For inactive N compounds, the reaction can be described using the following formula:

Some of the displacement reactions are irreversible, and the extracted component N become inert in the following charge / discharge cycles, however it can buffer against volume variation from the active materials^{45,47}.

The Gibbs free energy reaction can be used to calculate the reaction potential E_a versus lithium under equilibrium via the Nernst Reaction:

$$E_a = - \frac{\Delta G_m}{nF} \quad (3)$$

Where G_m is equivalent to the free energy of formation of product LiM_x , n is the number of electrons involved in the reaction and F is Faraday's constant.

When the displaced component is an active component towards lithium, it usually reacts with lithium at a different potential than the component M , and is usually at a lower potential. For the displaced element N this can be called a displacement reaction and addition reaction. Many active – active displacement reactions are irreversible after a few cycles and both components react with lithium as independent addition reactions⁴⁵.

2.5. Advanced alloy anodes for lithium ion batteries

By using the approaches that has been discussed, metallic alloys have become one of the promising alternative anode materials for high performance modern lithium ion batteries due to the much improved electrochemical performance. In this section, some of the alloy anodes that have good potential for high performance batteries will be discussed.

(A) Sb and Sb based composites

Antimony (Sb) reacts with lithium and undergoes alloying reaction to form Li_2Sb and Li_3Sb . Sb has a theoretical specific capacity of 660 mAh/g with the formation of Li_3Sb and

around 1890 mAh/cm³ of gravimetric capacity. During lithiation / delithiation, Sb exhibits a voltage profile of a well-defined plateau⁴⁵. Pure Sb electrodes suffer from rapid capacity fading and low cyclability due to the huge volume change experienced during lithiation. By using the approaches mentioned in Section 1.3, several reports have shown an improved electrochemical performance of Sb/ Sb composite electrodes. Dailly et al⁴⁹ reported the fabrication of Sb – graphite electrode with a stable performance of around 500 mAh/g. In addition, by using a Sb/carbon/graphite composite, excellent cycle life was exhibited, and 86% of its first charge capacity was retained after 100 cycles. In another report, Sb–carbon nanocomposites fabricated by HEMM (High Energy Mechanical Milling) have also shown improved electrochemical performance compared to conventional pure Sb electrodes.

Intermetallic compounds (A_xB_y) strategy has been shown to effectively improve the electrochemical performance of Sb based alloy anodes^{50, 51}. In these compounds, both components are reactive towards lithium, for example SnSb⁵² and AlSb⁵³, or active–inactive component such as Cu₂Sb⁴² and Cu₆Sn⁴³. Cu₂Sb is a Sb based intermetallic alloy that has been reported as one of the potential candidate for the lithium ion battery electrode. CuSb fabricated by HEMM method has reported a stable capacity of 290 mAh/g with good cyclability due to the good structural relationship and stability between the Cu₂Sb and the lithiated Li₂CuSb phase. Furthermore, the extruded Cu phase also provides good electronic conductivity during lithiation / delithiation, enables quick reaction kinetics, and acts as a buffer matrix. However, despite the stable capacity of the Cu₂Sb, it did not surpass the commercially available graphite electrode performance.

SnSb is one of the most studied alloy anodes due to the interesting electrochemical properties. Due to the ductile Sn phase that can alleviate volume expansion during cycling

and both Sn and Sb reacting at a different potential to lithium, so that while one component react to lithium, the other can acts as a buffer to reduce the volume expansion⁵². A hybrid SnSb / C nanocomposites has been reported which involves the transformation of micron sized tin and antimony powders into uniformly distributed 10 nm and 2-3 nm SnSb nanocrystallines in a carbon matrix by mechanochemical and electrochemical routes. The SnSb/ C nanocomposites are shown to have a superior electrochemical performance of 706 mAh/g with good Coulombic efficiency and capacity loss of only 19%. After 300 cycles, the nanocomposites still can deliver a capacity of around 550 mAh/g⁵⁴.

(B) Al and Al based composites

Aluminum and aluminum based compounds have been studied extensively as a possible anode material to replace lithium in the lithium batteries since early 1970. However, the use of aluminum based alloy in lithium ion batteries is rarely studied. From the binary phase diagram of Al–Li indicates that there are three types of alloys that can possibly be formed: AlLi, Al₂Li₃, and Al₄Li₉. Therefore, the maximum theoretical uptake of lithium in this alloy is 2.25 Li for each Al atom. Although this value is lower compared to the uptake of lithium in tin alloy (4.4 Li for each Sn alloy), due to the low atomic weight of Al, the highest theoretical capacity for Al alloy is 2234 mAh/g if Al₄Li₉ is reached. This value is much superior compared to the value for the theoretical capacity of tin. For the AlLi alloy, the theoretical capacity is 993 mAh/g. This makes aluminum based alloys an interesting anode materials for lithium ion batteries⁵⁵.

Similar to most alloy anodes, aluminum based alloy anodes also suffer from rapid capacity fade and irreversible capacity loss due to the rapid volume expansion. It has 96 %

volume change during lithiation and the capacity decline rapidly in only a few cycles. Intermetallic compounds strategy has been pursued for Al alloy, and Al based composites have shown improved electrochemical performance compared to the single pure Al electrode⁵⁵⁻⁶⁰.

Al-C, Al-Fe, and Al-Fe-C have been synthesized by using HEMM and shown improved electrochemical performance compared to pure Al alloy anodes⁵⁶. Fe is an inactive component and is believed to act as a buffer matrix to reduce the volume expansion of Al. Furthermore, the Al-Fe-C composite can deliver an initial capacity of 520 mAh/g and maintain a capacity of 255 mAh/g after 15 cycle. However, the capacity of this composite is still quite low due to the presence of the inactive component (Fe). The irreversible capacity loss is due to the breakage of graphite during the HEMM process.

Al-Sn is another aluminum based alloy that has very interesting properties for use as anode materials. Both Al and Sn are active components with LiAl having theoretical capacity of 993 mAh/g and LiSn having theoretical capacity of 994 mAh/g. Furthermore, Al-Sn is an immiscible alloy system, meaning that it will not form any intermetallic or solid solution phase structure. This property makes Al-Sn system a unique composite that would allow different lithiation / delithiation mechanism compared with those system containing intermetallic compounds⁵⁷. Al-Sn alloy has been synthesized using electron beam deposition resulting in tiny Sn particles dispersed homogeneously in the Al matrix. The electrode with a high Al content delivers a high initial discharge of 752 mAh/g, while the electrode with high Sn content is capable of delivering a stable specific capacity of around 300 mAh/g after 50 cycles. The improved electrochemical performance is believed to be

due to the improved reaction kinetics and lithium transfer rate in the nanostructure where the Sn nanoparticles are evenly distributed through the Al matrix⁵⁸.

Al-Sb alloy can potentially replace the commercial anode in lithium ion batteries. Al-Sb alloy is a zinc – blende type structure that provides a three dimensional interstitial space for lithium insertion⁵⁹. Lithium can be inserted in the open framework structure of the Al-Sb alloy followed by Sb extraction. Subsequently, the 2.73 lithium ions will further react with Sb to form Li_3Sb and Al. Finally, the lithium can also react with aluminum to form LiAl . This reaction is reversible during the delithiation process where both aluminum and antimony will reform Al-Sb alloy. Both components are active materials, with Sb (Li_3Sb : 660 mAh/g) and Al (LiAl : 993 mAh/g) both contributing to the overall capacity. Furthermore, due to reaction potential difference with lithium, the reaction with lithium will be done in a stepwise manner⁶⁰. Lithium ions will be inserted into the more reactive Sb first while the unreacted ductile Al will act as a buffer matrix.

Figure 1.7 shows the binary phase diagram of Al-Sb alloy. From the phase diagram it is shown that the synthesis of Al-Sb alloy resulted in formation of single phase of AlSb at around 1063°C with 50 wt. % Al content. Due to the high melting point of the AlSb phase in the phase diagram, synthesis of this alloy by using conventional casting methods could result in formation of impurities and metal oxides as oxygen reactivity is significantly increased at high temperature. High impurities and presence of oxides can be detrimental for the use of Al-Sb alloy as electrode in lithium ion batteries, therefore other synthesis methods must be pursued in order to successfully synthesize high purity Al-Sb alloy material. Mechanical Alloying is one of the synthesis method that has been investigated to synthesize Al-Sb alloy as an anode material. In this method, pure Al and pure Sb metal are

put in the ball milling chamber to be grinded. Due to the impact subjected by the balls, Al and Sb are mechanically bonded and form an alloy. However, this method results in a large size Al-Sb powder, and it has poor electrochemical performance with first cycle capacity of around 350 mAh/g and rapid capacity fade to 100 mAh/g after 4 cycles⁶⁰. To improve the battery performance of the Al-Sb alloy, other synthesis method must be investigated.

Figure 1.7. Binary phase diagram of Al – Sb⁶¹.

2.6. Melt Spinning

Melt spinning is a rapid solidification process with a typical cooling rate in the order of 10^6 K/s, and resulted in nanocrystalline or amorphous metallic phase structure with unique material properties compared to conventional casting method⁶². Unlike other rapid solidification process such as pulsed laser ablation (PLD) and gas atomization which are

relatively slow and intermittent processes, melt spinning is a high throughput and high scalability process, which can produce a large quantity of high purity materials, making this process feasible and scalable for industrial application. Furthermore, compared to other various chemical synthesis methods used to prepare alloy composites, melt spinning can deliver high purity metal alloy products with little to no impurities. The presence of impurities in an electrode is undesirable as they consume lithium irreversibly in the first discharge cycle and lead to low Coulombic efficiency.

Melt spinning process was first developed in early 1908 by Strange and Pim⁶³, and has been further extended and improved ever since^{64, 65}. As a form of rapid solidification process, melt spinning has been used for the production of polymer fibers⁶⁶ and metallic glasses⁶⁷. The precursor material is first melted by induction to molten liquid and then a stream of molten liquid is ejected through the nozzle by pressurized inert gas onto a rotating copper drum and pulled over the surface. The molten liquid rapidly cools and solidifies when in contact with the cold surface of copper drum, and result in either a nanostructure or amorphous phase features. A high cooling rate in the order of 10^6 K/s can be achieved in the melt spinning and the resulting products are ribbons with typical thickness of a few micrometers. This technique is a cost effective and industrial friendly process that is suitable for the mass production of high performance lithium ion batteries. The schematic process of melt spinning system is shown in Figure 1.8.

Figure 1.8. Schematic process of melt spinning system.

Recently, melt spinning system has been used to synthesize high performance alloy anodes for lithium ion battery system. SnSb alloy prepared by using melt spinning process demonstrated superior electrochemical performance compared to conventional method with good Coulombic efficiency and a reversible capacity of 860 mAh/g during the 40th cycle at a current density of 160 mA/g⁶⁸. Furthermore, the composite also demonstrated improved capacities at high C rates. The electrochemical performance improvement is due to the synergistic effect between the CNT scaffold and the nanocrystalline SnSb alloy, which improved the speed of lithium ion diffusion and acts as buffers against volume change and structural pulverization.

Si-Ti-Ni ternary alloy has also been synthesized by using melt spinning process⁶⁹. The melt spun alloy demonstrated a stable capacity above 900 mAh/g after 50 cycles and a high Coulombic efficiency of up to 99.7% during cycling. This superior performance is due to the presence of nano Si anode embedded in a $\text{Ti}_4\text{Ni}_4\text{Si}_7$ matrix. The $\text{Ti}_4\text{Ni}_4\text{Si}_7$ matrix

minimizes the maximum stress involved in the nano Si particles and mechanically confines Si expansion during lithiation by applying a compressive stress to the particles. The $\text{Ti}_4\text{Ni}_4\text{Si}_7$ matrix is also isolates nano Si from the liquid electrolyte due it is a good mixed conductor, and thus preventing unwanted side reactions that is responsible for the formation of SEI layer.

Al based materials Al-Si-Mn has been synthesized by using melt spinning with $\text{Al}_{55}\text{Si}_{40}\text{Mn}_5$ ⁷⁰ achieved a stable capacity of 600 mAh/g and $\text{Al}_{83}\text{Si}_{12}\text{Mn}_5$ ⁷¹ achieved a good cyclability of over 550 mAh/g after 50 cycles. The good electrochemical performance is due to the addition of Mn that could improve the solubility of Si in α – Al and prevented the crystal lattice from being destroyed. The presence of inert metallic glass in the structure also acts as a buffer against volume change during lithium insertion / extraction process^{70,71}.

Another Al-based system (Al–Si–Ni ternary alloy) has also been synthesized by melt spinning, with the $\text{Al}_{73}\text{Si}_{25}\text{Ni}_2$ samples ratio showed high Coulombic efficiency of 93% during cycling with first discharge capacity of 1400 mAh/g and a stable capacity of 661 mAh/g after 40 cycles, and the $\text{Al}_{68}\text{Si}_{25}\text{Ni}_7$ showed first discharge capacity of around 820 mAh/g and high cyclability of 780 mAh/g after 40 cycles⁷².

The ribbons is composed of nanoscaled α -Al, metallic glass (amorphous metal), and α -Si, in which the α -Al is a supersaturated solid solution of Si and Ni in fcc Al. The nanoscale α -Al embedded in the metallic glass matrix is beneficial to enhance the structural stability, restrain structure changes, and reduce the volume changes and pulverization during lithium insertion / extraction.

2.7. Summary

Due to ever increasing demand of high performance battery, the current commercially available graphite electrode has become insufficient to power modern day electronic devices and electric vehicles. Development of advanced battery materials with high energy density, high capacity, long cycle life, low cost and environmentally friendly is of utmost importance. Of all the candidates for graphite anode replacement, metallic alloy has huge potential due to the highest theoretical specific capacity compared to other candidates, and low operation potential versus Li. The drawback in using these alloy anodes is the large volume change during lithium insertion and extraction that can lead to irreversible capacity and low cyclability.

By combining different metal into composites, the large volume change can be minimized as the metals have different reaction potential with Li, while one of the metal react with Li and expands, the other metal can acts as a buffer matrix to reduce the volume expansion caused by the reaction with Li. Al-Sb, Sn-Sb, Cu-Sb are a few examples of metal alloys that has been investigated for use in lithium ion batteries.

Al-Sb alloy is one of the materials that can potentially replace the graphite electrode in lithium ion batteries. The high theoretical capacity of Al (990 mAh/g) and Sb (660 mAh/g), difference in reaction potential with Li between Al and Sb, and also the low cost of materials are the advantages of using Al-Sb alloy. However, due to the high temperature melting point of this alloy, it is quite difficult to successfully synthesize Al-Sb alloy with conventional casting method as it is prone to impurities and oxides formation. The presence of impurities in the electrode material is detrimental to the electrode performance, thus it must be minimized.

Until now, the synthesis of Al-Sb alloy has been done by using mechanical alloying, resulting in poor battery performance. The poor battery performance is due to the large volume change resulting in the electrode breakdown, and the introduction of defects sites into the electrode due to the mechanical alloying method. Lithium could be inserted into the defect sites and then bound tightly to a part of host atoms at defect sites present within the bulk or on the surface of the electrode. The irreversible insertion of lithium will result in rapid capacity fade and low cyclability.

In order to improve the battery performance of Al-Sb alloy, other alternative synthesis method must be pursued. The proposed method is to use melt spinning to synthesize Al-Sb alloy as this method can result in high purity materials with unique properties. The rapid solidification process of the melt spinning has been shown to produce high purity products with unique morphologies that improved the battery performance of several alloy anodes such as SnSb, Al-Si-Ni, Al-Si-Mn, and Si-Ti-Ni. To the best of our knowledge, the use of Al-Sb alloy as anodes for lithium ion batteries has rarely been studied. Therefore, in this report, Al-Sb alloy synthesized by melt spinning will be fabricated and investigated for the morphological and electrochemical properties, in order to evaluate the capability for potential replacement as anode in lithium ion batteries.

Chapter 3

Experiment Methodology

3.1. Experiment Work Flow Chart

Figure 3.1. Experimental Work Flow Chart.

3.2. Preparation of melt spun Al – Sb alloy

Antimony powder (99.9%, Sigma Aldrich) and aluminum powder (99.9%, Sigma Aldrich) were weighed in various weight ratio, $\text{Al}_x\text{Sb}_{1-x}$ (where $x = 2, \dots, 8$) and then made into pellets by cold pressing. The nanostructured Al–Sb alloy was prepared from the cold

pressed pellets using a single roller melt spinner (Edmund Buhler GmbH., Melt Spinner SC) with a 20 cm diameter copper wheel in argon filled chamber. The distance between the bottom of the nozzle and the surface of the copper wheel was set at 0.5 mm, and the rolling distance of the wheel was 60 Hz. The precursor was induction melted to molten liquid and then pressure ejected through the slotted nozzle. Upon contact with the water-cooled wheel, the molten liquid rapidly solidified into very thin flakes.

The as-spun Al-Sb flakes were then triturated using a mortar grinder mill (Retsch, RM100) for 1 h to ensure a fine grinding. The obtained fine particles was then mixed with the acid treated CNTs (P3-SWNT, Carbon Solutions) in a weight ratio of 9:1 and dispersed in N-methylpyrrolidinone (NMP) and ultrasonicated for 1 h. It was then left to stir on a magnetic stirrer at 400 rpm for 2 days to ensure homogeneous mixing. The dispersion of the CNTs in solution is known to be a challenge as van der Waals interactions gives rise to a strong tendency for the CNTs to agglomerate, bundle and entangle⁷³. Several authors have shown the possibility of dispersing CNTs in amide based solutions, including NMP⁷⁴⁻⁷⁶. Hence, NMP was chosen as the dispersing agent for this work as it is also the solvent to prepare the electrode material.

3.3. Characterization

Phase structures of the nanocomposites were investigated by powder X-ray diffraction (XRD) (Bruker AXS, D8 Advance) using Cu K α radiation ($\lambda = 0.15418$ nm) over 2θ range of $10^\circ - 80^\circ$. Ion Polishing was used to cut the ribbon samples to produce the cross section morphology of the ribbons. Tapping density was measured by placing the grinded powder sample into 1.5 ml bottle and tapped 1000 times to measure the mass of the powder. Field

emission scanning electron microscope (FESEM) (JEOL, JSM-7600F) with energy dispersive X-ray spectroscopy (EDS) attachment were used for microstructure and elemental composition analysis of the melt spun flakes and nanocomposites before and after cycling. For microstructure analysis of the composite after cycling, the cell was disassembled in the glove box, washed with dimethyl carbonate (DMC) to remove any residual electrolytes and left to dry prior to characterization.

3.4. Electrochemical Measurements

The anode was fabricated by mixing the AlSb, CNT, and poly(vinylidene fluoride) (PVDF) dissolved in N-methylpyrrolidinone (NMP) at a weight ratio of 80:10:10. Pure Al and pure Sb was also tested for battery performance as comparison by directly mixing the pure Al / Sb powder (99.9%, Sigma Aldrich) with CNT and poly(vinylidene fluoride) (PVDF) dissolved in N-methylpyrrolidinone (NMP) at a weight ratio of 80:10:10. The slurry was then pasted onto the copper foil and dried in vacuum at 55° C for 8 h. CR2032 coin-type batteries in the half-cell configuration were then assembled in an argon-filled glove box with moisture and oxygen content less than 1 ppm. Lithium foil is used as the counter electrode and reference electrode, Celgard 2400 membrane as the separator and a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w w⁻¹) as the electrolyte. Cyclic voltammetry was performed with an electrochemical workstation (CHI 660C) at a scan rate of 0.5 mV/s in the potential range of 0.05 – 3.0 V. The cells were cycled galvanostatically between 0.05 and 3.00 V (vs. Li/Li⁺) at various current densities using the NEWARE multi-channel battery test system.

Chapter 4

Results and Discussion

4.1. Characterization of Al-Sb alloy ribbons

The Al-Sb alloy synthesized by melt spinning resulted in thin ribbons with thickness of around 8 – 10 μm . the length of the ribbons varies according to the sample composition ratio. The samples are denoted as AlXSbY with X is the weight percent ratio of Al and Y is the weight percent ratio of Sb, with X and Y ranging from 20 to 80 wt.%. The length of the ribbon samples varies according to the samples composition ratio. As the Al composition in the ribbons increases, so does the ribbons length. In the Al80Sb20 sample, the ribbons were around 10 cm in length, while in Al20Sb80 samples the ribbons were more like flakes of around 0.5 cm in length.

The ribbon samples with high Al content (Al = 60 to 80 wt.%) were observed to have high ductility with the highest ductility observed in the Al80Sb20 samples, while the ribbons with high Sb content (Sb = 60 to 80 wt.%) were brittle, with the Al20Sb80 samples being very brittle and easily broken.

To observe the morphological properties of the Al-Sb alloy ribbons, the ribbons were ion polished to examine the cross section of the ribbons. To identify the phases present in the ribbons, Backscattered Electron Image (BEI) mode was used for the FESEM characterization. Figure 4.1 shows the BEI FESEM images of the ribbon cross section from Al80Sb20 to Al20Sb80 showing the phases present in the samples.

Figure 4.1. The BEI images of the cross section morphologies of Al-Sb alloy with different ratios: a) Al₈₀Sb₂₀, b) Al₇₀Sb₃₀, c) Al₆₀Sb₄₀, d) Al₅₀Sb₅₀, e) Al₄₀Sb₆₀, f) Al₃₀Sb₇₀, and g) Al₂₀Sb₈₀.

In the BEI mode, the phases can be detected and observed due to the contrast difference between the phases. The contrast difference is due to the difference of atomic number (Z contrast) between the elements, with the heavier elements with high atomic number appeared brighter in contrast compared to the lighter elements with low atomic number. AlSb phase appeared the brightest as the heaviest compounds, with Sb appeared darker and Al the darkest. The phases present were also confirmed with Energy Dispersive X-ray (EDX) characterization.

Figure 4.1a shows the phases present in the Al₈₀Sb₂₀ sample. The phases were identified to be AlSb and α -Al phase. The microstructure is comprised of AlSb phases that are embedded in the matrix of α -Al grains. The AlSb plates are around 1 μm in size, and are distributed either in clusters or separately distributed in the matrix. Figures 4.1b and 4.1c are images obtained for samples with increased Sb composition ratio, where the AlSb plates present in the structure increased in number but decreased in size. In the Al₇₀Sb₃₀ sample, some smaller AlSb phases of around 0.1 to 0.5 μm are present along with the 1 μm plates, while in the Al₆₀Sb₄₀ samples, the smaller AlSb phases are more numerous with only a few of the bigger 1 μm plates observable. The matrix is composed of α -Al grains and residual Sb grains. Figure 4.1d shows the image obtained for the Al₅₀Sb₅₀ samples. The AlSb phases are observed to be well dispersed throughout the structure with around 0.1-0.5 μm in size and surrounded by α -Al grains and residual Sb grains matrix. While the AlSb phase in the Al₇₀Sb₃₀ and Al₈₀Sb₂₀ are concentrated in clusters, the AlSb phases in Al₅₀Sb₅₀ are well dispersed in the structure.

Figures 4.1e, f, and g show the cross section image of the samples with high Sb composition ratio, and correspond to Al₄₀Sb₆₀, Al₃₀Sb₇₀, and Al₂₀Sb₈₀, respectively.

The FESEM images of these samples reveal that their morphologies are very different compared to that of Al50Sb50 to Al80Sb20 samples. The microstructure mainly consists of large Sb phases embedded within the matrix comprising of AlSb grains and some residual α -Al grains. The Sb grains observed in Al40Sb60, Al30Sb70, and Al20Sb80 samples are about 0.2 to 1 μm in size and are distributed in clusters throughout the structure.

Compared to other samples, the Al50Sb50 has well distributed AlSb phase throughout the microstructure and it is slightly smaller in size compared to other samples with different composition ratio. From the available data, we can assume that the reason for the well dispersed and smaller phase size of AlSb is due to the sufficient amount of both Al and Sb element in the melt to form a well dispersed AlSb phase in Al50Sb50 samples. When there is not enough amount of both Al and Sb in the melt to form AlSb phase, it will result in formation of AlSb phase that is clustered in some areas instead of well distributed throughout the microstructure. It is possible that as the temperature rapidly cooled down from the melt, the clustered AlSb phases did not have time to disperse and instead agglomerate and form together into a larger AlSb phase.

It is of interest to note that the shape of the AlSb phases are dendrite-like, while in conventional ingot cast Al-Sb alloy with ratio of 1:1, the AlSb phases are needle-like with 10 – 15 μm in width and 50 – 100 μm in length with a matrix of α -Al grains surrounding the AlSb phases, as shown in Figure 4.2⁷¹.

Figure 4.2a) FESEM BEI images of the Al₅₀Sb₅₀ cross section ribbon samples, b) Optical Microscope of conventional cast Al-Sb alloy showing black AlSb needle like particles and Al matrix⁷¹.

According to the binary Al-Sb phase diagram⁶¹, AlSb phase is congruently formed from the melt at 1062° C and has a cubic ZnS – type structure. Under conventional conditions, when the melt started to cool down, AlSb phase is formed first and grouped together to grow into coarse needle-like shape, and when the temperature is further lowered below the eutectic temperature the eutectic reaction occurs. However, in melt spinning where rapid solidification process occurs, the AlSb phase formation behavior is very different compared to the conventional melting conditions. The rapid cooling rates on the liquid metal induced a large kinetic under-cooling and render the metallic melt thermodynamically metastable and can be subjected to a range of non-equilibrium solidification effects. The growth of AlSb grains are repressed in the rapid solidification process such as melt spinning and the size of the particles is able to minimized to 0.1 to 1 μm in size compared to the 10 to 15 μm found in conventionally cast AlSb alloy. The smaller grain size of the melt spun samples is beneficial to the overall electrochemical performance due to the shorter Li diffusion path.

In the conventional cast Al-Sb alloys (Al: Sb = 1:1), the alloy structure is consisted of AlSb phases that are surrounded in α -Al phase, which is similar to the phase composition found in our melt spun Al50Sb50 samples. This behavior suggested that rapid solidification process such as melt spinning has little effect in the phase composition of the Al-Sb alloy.

The phase composition of the high Al content in the Al60Sb40 samples to Al80Sb20 samples is similar to the Al50Sb50 samples with AlSb phases embedded in α -Al matrix. However, in the high Sb content ratio of the Al40Sb60, Al30Sb70, and Al20Sb80 samples, the AlSb phase instead formed a matrix surrounding Sb grains. This is probably due to the low amount of Al content present in the melt, so that when rapidly cooled, the high content of Sb in the melt clustered together and formed individual grains.

The ribbons samples were then grinded into powder by using mortar grinder mill in order to characterize their electrochemical performances. The resulting powder is around 0.5 – 3 μm in size, as shown in Figure 4.3.

Figure 4.3. FESEM images of the grinded melt spun powder Al50Sb50 samples.

In order to further characterize the physical properties of the samples, tap density measurements were performed for all of the samples. The highest tap density is 1.89 g/cm^3 from the Al50Sb50 samples and the lowest is 1.65 g/cm^3 from the Al80Sb20 samples. Table 4.1 shows the tap density measurements for all the samples.

Samples	Tap density (g/cm^3)
Al80Sb20	1.68
Al70Sb30	1.70
Al60Sb40	1.77
Al50Sb50	1.83
Al40Sb60	1.82
Al30Sb70	1.80
Al20Sb80	1.72

Table 4.1. Tap density measurements for all grinded melt spun samples powder.

To confirm the phases present in the samples, XRD characterization was done on each composition samples. Figure 4.2 shows the XRD patterns for the various grinded Al – Sb ribbon samples from Al80Sb20 samples to Al20Sb80 samples. The results confirmed the formation of the tetrahedral AlSb phase (JCPDS 06 – 0233) and residual pure Al or pure Sb phase. From the XRD results no peaks corresponding to impurity phases are observable, confirming the high purity of the sample.

The phase composition in the grinded Al-Sb ribbon samples changes depending to the ratio of Al and Sb precursors. In Al-rich samples, the presence of α -Al peaks increases with increasing Al content due to the high amount of unreacted Al precursor. In Al50Sb50 samples, the phases present are AlSb and α -Al, which is similar to the conventional ingot cast AlSb alloy with 1:1 ratio. This result confirmed that the rapid solidification process

such as melt spinning does not significantly change the phase composition of the alloy samples.

Rietveld refinement was also performed on the XRD data to calculate the quantitative composition of the melt spun samples, and the results are summarized in Table 4.2. Table 4.2 shows the weight percent of the individual phases of AlSb, Al and Sb in the various samples. With increasing content of Al, the weight percent of Al increased while weight percent of AlSb decreased. In Al50Sb50 samples, the phase composition consists of about 90% AlSb phase and 10% Al phase with Al acting as a matrix. In the Sb rich samples starting from Al40Sb60 to Al20Sb80 samples, the weight percent of Sb increases with increasing Sb ratio, while the AlSb content and Al content decrease with increasing Sb ratio. The Al50Sb50 samples have the highest amount of AlSb weight percent compared to other samples.

Figure 4.2. XRD patterns of the Al – Sb alloys with various composition ratios.

Samples	wt % AlSb	wt % Al	wt % Sb	Calculated composition	
				Al at%	Sb at%
Al80Sb20	71.23	29.77	0	78.53	21.47
Al70Sb30	82.14	17.86	0	69.08	30.92
Al60Sb40	85.35	14.65	0	58.03	41.97
Al50Sb50	89.78	10.22	0	47.45	52.54
Al40Sb60	86.81	4.07	9.12	38.55	61.44
Al30Sb70	84.13	3.94	12.07	32.8	66.2
Al20Sb80	81.15	0	18.85	15.98	84.02

Table 4.2. Rietveld refinement calculation of the XRD results.

The lattice parameter from the refinement results are presented in Table 4.3. The biggest lattice parameter of α Al is of 0.4046 nm which is less than pure α -Al lattice parameter of 0.4049 nm^{12,70}. The Al phase belongs to the space group of $Fm-3m$ cubic system, while Sb is a rhombohedral $R3m-h$ system and AlSb is zinc blende $F43m$ system. The lattice parameter of Al increased with increased Al ratio, while the lattice parameter of AlSb is optimum at Al50Sb50 ratio samples and decreased by the addition of either Al / Sb into the structure.

Samples	a Lattice parameter (nm)			Crystallite size (nm)		
	Al	Sb	AlSb	Al	Sb	AlSb
Al80Sb20	0.4046	0	0.6128	63.2	0	85
Al70Sb30	0.4043	0	0.6130	58.7	0	87.4
Al60Sb40	0.4043	0	0.6131	58.1	0	89.7
Al50Sb50	0.4042	0	0.6135	57.3	0	91.6
Al40Sb60	0.4041	0.4304	0.6133	55.6	12.1	90.3
Al30Sb70	0.4040	0.4304	0.6133	54.2	14.3	90.1
Al20Sb80	0.4041	0.4309	0.6131	55	16.2	88.8

Table 4.3. Lattice parameter and crystallite size of the melt spun samples obtained from the XRD refinement results.

The crystallite size of the samples shown in Table 4.3 can be calculated by using Scherrer's formula:

$$\beta \times \cos (\theta) = 0.91 \times \lambda / D \quad (4)$$

Where β is the full width at half maximum length (FWHM) of the reflection peak, θ is the Bragg angle of the diffraction peak considered, λ is the wavelength of the X-ray used. The crystallite size for the Al phase increased with the addition of Al in the structure, while the crystallite size of the AlSb phase is the highest for the Al50Sb50 sample and started to decrease with either addition of more Al or more Sb in the composition ratio. The lattice parameter and crystallite size calculation for the Sb phase in the Al50Sb50 to Al80Sb20 cannot be done as there are no Sb peak recorded in the XRD results for these samples.

4.2. Electrochemical Performance of Al – Sb alloy

To evaluate the potential of the Al – Sb alloy synthesized by melt spinning as anode for lithium ion batteries, a series of electrochemical studies were performed based on the half – cell configuration. Figure 4.3 shows the comparison of the various Al–Sb alloys discharge capacity performance with CNT as additives. The electrode performance was evaluated galvanostatically at current density of 100 mA/g.

Figure 4.3. Comparison of discharge capacity of all the melt spun Al – Sb samples with CNT as additives.

From Figure 4.3, it is observed that all the Al – Sb samples could withstand repeated cycling until the 80th cycle with acceptable performance. The poorest performance came from the Al80Sb20 sample with the first discharge capacity of 475 mAh/g and huge irreversible capacity loss of around 70%, and after 20 cycles the capacity is only around 100mAh/g. The best battery performance came from the Al40Sb60 sample with first discharge capacity of 635 mAh/g and was able to maintain good cycling performance of 504 mAh/g after 80 cycles. The Al50Sb50 sample also has a good performance with first

discharge capacity of 600 mAh/g and after 80 cycles was able to maintain good capacity of around 470 mAh/g.

The volumetric specific capacity for the melt spun samples was calculated by using this following formula: volumetric specific discharge capacity (mAh/cm^3) = the tap density of active materials (g/cm^3) $\times$ gravimetric specific discharge capacity (mAh/g). Table 4.4 shows the volumetric specific discharge capacity for all samples, with the Al50Sb50 sample having a high tap density of $1.83 \text{ g}/\text{cm}^3$ achieving the highest volumetric capacity of $1129 \text{ mAh}/\text{cm}^3$, the Al80Sb20 sample with the lowest tap density of $1.68 \text{ g}/\text{cm}^3$ achieving a volumetric capacity of $758 \text{ mAh}/\text{cm}^3$.

Samples	Tap density (g/cm^3)	Discharge capacity (mAh/g)	Volumetric discharge capacity (mAh/cm^3)
Al80Sb20	1.68	451	758
Al70Sb30	1.70	498	846.6
Al60Sb40	1.77	600	1062
Al50Sb50	1.83	617	1129
Al40Sb60	1.82	616	1121
Al30Sb70	1.80	592	1066
Al20Sb80	1.72	502	863

Table 4.4. Discharge capacity and volumetric discharge capacity for all melt spun samples.

The first charge and discharge capacities with a Coulombic efficiency for the first cycle from all samples are presented in Table 4.5. It can be observed that the melt spun samples have high 1st Coulombic efficiency, with the Al80Sb20 sample having achieved a first Coulombic efficiency of 76% being the lowest compared to all samples, while the highest

Coulombic efficiency is achieved by the Al50Sb50 samples with 87% efficiency. The Al80Sb20 sample demonstrated very poor cyclability with only 21% of cycle retention capacity at 80 cycles.

Samples	First charge capacity	First discharge capacity	1st Coulombic efficiency (%)	Cycle retention of discharge capacity
Al80Sb20	588 mAh/g	451 mAh/g	76	21 % (after 80 cycles)
Al70Sb30	632 mAh/g	498 mAh/g	78	54 % (after 80 cycles)
Al60Sb40	694 mAh/g	600 mAh/g	86	60 % (after 80 cycles)
Al50Sb50	708 mAh/g	617 mAh/g	87	70 % (after 80 cycles)
Al40Sb60	720 mAh/g	616 mAh/g	85	75 % (after 80 cycles)
Al30Sb70	701 mAh/g	592 mAh/g	84	57 % (after 80 cycles)
Al20Sb80	643 mAh/g	502 mAh/g	78	48 % (after 80 cycles)

Table 4.5. First charge / discharge capacity, Coulombic efficiency and cycle retention comparison for all melt spun Al-Sb samples.

The melt spun samples exhibited a good cycle retention capabilities with Al40Sb60 samples able to maintain 75% of the first discharge capacity after 80 cycles and Al50Sb50 also able to maintain 70% of the first discharge capacity after 80 cycles. This suggested that the melt spun samples demonstrated very good electrochemical reversibility. By considering the XRD refinement results and the FESEM characterization done on these samples, it is possible that the presence of small size and well distributed AlSb grains helped improve the electrochemical performance of this material.

By referring to the FESEM and Rietveld refinement results, the poor performance of the Al80Sb20 samples could be due to the lower amount of AlSb phase of around 70 wt.% which is distributed in clusters and the high amount of individual Al matrix that surrounds

the AlSb phase. The slower diffusion kinetics of Al could hinder the lithium diffusion into AlSb phase and lower the battery performance.

The reason that the samples with different composition ratio have different 1st cycle Coulombic efficiency might be caused by the difference in the amount of unreacted element such as Al and Sb in the samples. Table 4.6 below shows the 1st Coulombic efficiency comparison between the samples and the calculated composition of each samples. It can be seen that the lower 1st cycle Coulombic efficiency occurred at the samples with higher amount of unreacted Al and Sb phase.

Samples	wt % AlSb	wt % Al	wt % Sb	Calculated composition		1st Coulombic efficiency (%)
				Al at%	Sb at%	
Al80Sb20	71.23	29.77	0	78.53	21.47	76
Al70Sb30	82.14	17.86	0	69.08	30.92	78
Al60Sb40	85.35	14.65	0	58.03	41.97	86
Al50Sb50	89.78	10.22	0	47.45	52.54	87
Al40Sb60	86.81	4.07	9.12	38.55	61.44	85
Al30Sb70	84.13	3.94	12.07	32.8	66.2	84
Al20Sb80	81.15	0	18.85	15.98	84.02	78

Table 4.6. Comparison between 1st Coulombic efficiency and the composition of each samples.

A low 1st Coulombic efficiency can be attributed to the trapping of lithium ions inside the structure due to the slow lithium release kinetics, formation of highly stable lithiated compounds, and strong bonding with less coordinated atoms at defect sites.

Previous study by M. Stjerndahl *et al*⁵³ has shown that pure alloy anodes such as Al and Sb tend to suffers from low 1st Coulombic efficiency due to the irreversible

consumption of lithium ions into the structure and large volume change caused by lithium insertion / extraction. Due to the huge volume change and a transformation of structured occurred during lithium insertion/ extraction, Li can be trapped permanently at the defect sites that are present at the surface, interface, or grain boundaries of the alloy anodes.

Therefore, it can be assumed that the amount of unreacted Al and Sb phase present in the samples composition can contribute to the 1st Coulombic efficiency in the samples, with a higher amount of unreacted Al and Sb phase resulted in a lower 1st Coulombic efficiency in the samples.

The melt spun samples were also tested with respect to their charge rate (C rate) in order to accurately compare the battery performance between the samples. Figure 4.4 shows the battery performance comparison of pure Al, pure Sb, Al70Sb30, Al50Sb50, and Al30Sb70 with their respective C rate. Due to the different Al and Sb composition ratios, the C rate calculation is different for each sample. In Al50Sb50, 1C is equivalent to 825 mA/g, while in Al70Sb30 and Al30Sb70, 1C is equivalent to 891 mA/g and 759 mA/g respectively. In the comparison, all of the samples were cycled at a current rate of 0.1C.

The pure Al and pure Sb samples showed poor electrochemical performance with rapid capacity fading after 20 cycles. The pure Al samples have first discharge capacity of 700 mAh/g but quickly drop to 15 mAh/g after 20 cycles. Similar behaviour is also observed for the pure Sb samples, which quickly drop to 12 mAh/g after 20 cycles after the first discharge capacity of 560 mAh/g. The first Coulombic efficiency of the pure Al samples is ~78% and for the Sb samples The Coulombic efficiency is around 76%. The reason for the poor performance of the pure Al and Sb samples is due to the large volume change occurred

during lithium insertion / extraction from the structure, which cause the breakdown of the active material and electrical isolation from the current collector.

Figure 4.4. Battery performance comparison between pure Al, pure Sb, Al70Sb30, Al50Sb50, and Al30Sb70 samples.

The Al50Sb50 samples was cycled at 0.1 C rate (82.5 mA/g) and obtained first discharge capacity of 670 mAh/g with stable capacity of 560 mAh/g after 80 cycles. The battery performance of the Al50Sb50 is the best compared to Al30Sb70 samples which is cycled at 0.1 C rate of 89.1 mA/g and Al70Sb30 samples cycled at 0.1 C rate of 75.9 mA/g,

which is consistent with previous battery performance that is cycled at current rate of 100 mA/g.

In summary, by observing the battery performance behaviour of the all the melt spun Al-Sb samples from Al₂₀Sb₈₀ to Al₈₀Sb₂₀, the samples with high content of Al compared to Sb ratio such as Al₈₀Sb₂₀ and also the samples with high content of Sb such as Al₂₀Sb₈₀ did not perform very well in terms of battery performance compared to other Al – Sb composition ratios. Based on the XRD refinement results, the samples that are performing well had high amount of AlSb phase in the structure such as Al₅₀Sb₅₀ samples with 89 wt.% AlSb phase and Al₄₀Sb₆₀ samples with 86 wt.% AlSb phase, while the samples with lower AlSb phase such as Al₂₀Sb₈₀ with and Al₈₀Sb₂₀ did not perform as good as other samples. The poor electrochemical performance can be attributed to the high amount of unreacted Al and Sb phase in the structure, which could result in trappings of lithium inside the host alloy due to the slow lithium release kinetics from the individual Al and Sb phase. The performance of the Al – Sb alloy synthesized by melt spinning is still well within the theoretical capacity of Sb (660 mAh/g) and Al (990mAh/g).

In order to further examine the battery performance, a multi rate battery performance was performed from discharge rate of 100 mA/g to as high as 1600 mA /g. The Al₄₀Sb₆₀, Al₅₀Sb₅₀, and Al₆₀Sb₄₀ samples were investigated for the multi rate battery performance as these three samples gave the best performance, and the results are shown in Figure 4.4.

Figure 4.4. Multi rate battery performance of Al – Sb samples with compositions of a) Al40Sb60, b) Al50Sb50, and c) Al60Sb40.

The Al40Sb60 samples in Figure 4.4a demonstrated a good high rate performance with initial capacity of 670 mAh/g with current density of 100 mA/g. With increasing current density of 200 mA/g, 400 mA/g, 800 mA/g, and 1600 mA/g, the sample could still maintain good capacity of 530, 425, 310, and 247 mAh/g, respectively, with high Coulombic efficiency of more than 98% could be attained. The Al40Sb60 performed the best compared to the other samples such as Al50Sb50 in Figure 4.4b and the Al40Sb60 in Figure 4.4c.

Previous studies by Gaberscek *et al.*⁷⁷ and Johns *et al.*⁷⁸ have demonstrated that the enhanced rate performance can be obtained by controlling the composition and the structure of the composites and size miniaturization of the active materials. As the AlSb phase is very well distributed throughout the structure and of small size (0.1 - 1 μ m), it will result in shorter lithium ion diffusion path and faster ionic transport.

The Al40Sb60 performed slightly better in terms of electrochemical performance compared to Al50Sb50. This could be due to the higher amount of Al phase in the Al50Sb50 of around 10% compared to around 4% in the Al40Sb60 samples. Al has very slow lithium diffusion kinetics compared to other alloys, and the solubility of lithium in Al is about 1% in 373K⁵⁷.

In order to understand the contribution of CNT to the battery performance, a comparison between the Al-Sb alloy with CNT and Carbon Black were performed. CNT is known to react with lithium, although the capacity contribution of CNT to the overall battery performance is quite small, which is less than 150 mAh/g.

Figure 4.5 compares the battery performance of Al-Sb alloy with CNT and with Carbon Black additives. It is shown that by combining Al-Sb alloy with CNT, an improved battery performance and reduced initial irreversible capacity loss can be obtained compared to the Al-Sb alloy with Carbon Black.

Figure 4.5. Comparison of battery performance between CNT and Carbon black for a) Al40Sb60, b) Al50Sb50, and c) Al60Sb40.

Previous study by S. Fan *et al.*⁶⁷ indicates that CNT can provide cooperative enhancement for the battery performance in SnSb alloy anodes. CNT has a mesh – like network that can wrap the electrode particles inside the structure, thus facilitate a highly percolated pathway of electrons transport from the electrode particles and significantly improves the electrical conduction. The large irreversible capacity loss that is caused by volume variation can be minimized due to the inherent good mechanical flexibility of the CNT and the void spaces present in between the CNT mesh – like network⁸⁰.

Figure 4.6. a) Cyclic voltammetry profile of the first 4 cycles of Al50Sb50 alloy, b) Galvanostatic charge / discharge profiles at a current density of 100 mA/g.

Figure 4.6 shows the cyclic voltammetry profile of the Al50Sb50 samples and the galvanostatic charge / discharge profiles at current density of 100 mA/g. From the cyclic voltammetry profile in Figure 4.6a, a large peak around 1 V to 0.5 V is observed. This peak is the lithium absorption into the interstitial sites of the zinc blende AlSb framework to form a metastable Li_xAlSb phase:

At potential slightly below 0.5 V, further reaction with Li caused some of the AlSb phase to extrude Sb particles from the AlSb framework, in which the Sb particles first react with 2 Li^+ ions and then absorb another Li^+ ion to form Li_3Sb . At 0.24 V, aluminium particles will react with lithium to form LiAl . De-alloying of Li_3Sb occurs at around 1.1 V followed by the de-alloying of ternary phase of Li_xAlSb at around 1.8 V, thereby restoring AlSb phase. Restoration of AlSb phase is beneficial as it can help to reduce the

agglomeration of Sb particles into larger grains which can be detrimental to the battery performance. Previous studies in other systems such as SnSb⁶⁸ and InSb⁸¹ revealed that the agglomeration of particles is one of the key reasons for poor cycle stability in intermetallic alloy based materials.

Figure 4.6b shows the charge / discharge voltage profiles for the Al50Sb50 samples tested at 100 mA/g current density. In the charge / discharge voltage profiles, the potential plateaus were consistent with the CV results. The gently sloping plateau that occurs in between 1.0 V to 0.5 V accounts for the most of the reversible capacity is due to the contribution of the AlSb phase. Below 0.5 V, the capacity contribution came from the formation of Li₃Sb. As AlSb contributes the most to the overall battery capacity, the restoration of AlSb phase after lithiation is of significant importance to the cycle life and battery performance of the Al-Sb alloy.

4.3. Comparison with other Al based materials

Compared to other Al based materials such as mechanically alloyed Al-Sb⁶⁰ and Al-Fe⁵⁶ materials, the melt spun Al-Sb samples exhibited much improved capacities and cyclability performance. The melt spun samples exhibited high Coulombic efficiency and much improved cycle retention.

In the mechanically alloyed Al-Sb previously reported⁶⁰, the capacity is around 300 mAh/g with current density of 100 mA/g with particle size around 5-7 μm . They suggested that the poor electrochemical performance is due to the introduction of defects into the structure by mechanical alloying. Lithium can insert and bond strongly into the defects site in the structure thus lowering the overall electrochemical performance.

When compared to other melt spun Al based materials reported before such as the ternary system of Al-Si-Mn^{70,71} and Al-Si-Ni⁷², the melt spun Al-Sb samples demonstrated comparable electrochemical performance and cyclability. The Al-Si-Mn has reported to be able to sustain very stable capacity of over 800 mAh/g after 40 cycles.

4.4. Post mortem characterization of melt spun Al – Sb alloy

In order to further examine the capability and stability of the Al-Sb alloy synthesized by melt spinning and to understand the mechanism behind performance difference of each Al: Sb composition ratio, lithium ion battery cells cycled at 100 mA/g current density for 100 cycles were opened in the glove box and post mortem studies were done using FESEM. The results are shown in Figure 4.7. In the Al₂O₈ samples, large cracks were seen and some active material particles were detached when the cell was opened in the glove box. As shown in Figure 4.7a, a closer observation by FESEM revealed some of the active electrode material have detached from the current collector, due to the severe volume changes occurring in the electrode.

The breakage of material and the loss of contact to the current collector caused rapid capacity fade and irreversible capacity loss demonstrated in battery performance test in Figure 4.3. The electrode breakage could be due to the high amount of unreacted Sb in the structure, as the lithium insertion into the Sb structure to form Li₃Sb results in huge volume expansion of 200 %⁸ which can disrupt the structural integrity of the electrode.

Figure 4.7. FESEM images of the Al – Sb alloy electrode material after 100 cycles at 100 mA/g current density. a) Al₂₀Sb₈₀, b) Al₄₀Sb₆₀, c) Al₅₀Sb₅₀, d) Al₆₀Sb₄₀ and e) Al₈₀Sb₂₀.

In Figure 4.7 b-d, after the battery cells were opened in the glove box, from the naked eye the electrode is still fully attached to the current collector with only small cracks visible. Further observation by FESEM revealed that cracks with around 3-5 μm in length and around 0.2 to 0.5 μm in width occurred along the surface of the electrode. There are no observable detachment of active material from current collector, therefore suggesting that the volume changes caused by lithium insertion / extraction formed cracks in the surface of the electrode, the impact is somewhat minimized as the active electrode material is still fully intact and no significant breakage of material observed.

In Figure 4.7e, the Al80Sb20 showed large amounts of cracks in the surface of the electrode. When opened in the glove box, some of the electrode already peeled off from the electrode and large cracks could be seen by naked eye. However, the cracking and the peeling off from current collector is not as severe as the Al20Sb80 samples. The electrode cracking behaviour in all of the samples corresponds with the electrochemical performance.

In order to obtain a better understanding of the Al-Sb alloy battery performance, after lithiated for 100 cycles, the battery cells were opened in the glove box and taken out from the current collector to observe the changes in the phases using XRD after lithium insertion / extraction. Figure 4.8 shows the XRD diffraction patterns for the Al – Sb alloy from Al20Sb80 to Al80Sb20 after 100 cycles at 100 mA/g current density. Peaks corresponding to LiAl and Li₃Sb phases cannot be detected in the XRD results, as both domains are too small to be identified in the XRD spectra⁶⁰. During lithium insertion, lithium ions first enter the interstitial sites of the AlSb zinc blende framework ($F - 43m$) to form Li_xAlSb up until 0.5 V. Below 0.5 V, the Sb particles from the AlSb structure started to be extracted out from the AlSb structure to react with the lithium to form Li₃Sb.

Figure 4.8. XRD characterization of the lithiated Al – Sb alloy anodes cycled at 100 mA/g current density for 100 cycles.

In order to achieve good cycle life and stability, the restoration of the AlSb phase is of significant importance due the huge contribution of this phase to the overall battery capacity. However, as shown in XRD results in Figure 4.8, not all of the Al and Sb particles that have been extracted out from AlSb phase during lithiation reform back into the original AlSb structure. In the Al₂₀Sb₈₀ sample, only weak AlSb phase peak is found in the XRD patterns, with high amount of Sb peaks present.

Samples	Before lithiation			After lithiation		
	wt % AlSb	wt % Al	wt % Sb	wt % AlSb	wt % Al	wt % Sb
Al80Sb20	71.23	29.77	0	54.16	35.97	9.87
Al70Sb30	82.14	17.86	0	74.32	16.07	9.61
Al60Sb40	85.35	14.65	0	77.02	14.90	7.18
Al50Sb50	89.78	10.22	0	80.75	9.89	9.36
Al40Sb60	86.81	4.07	9.12	82.63	3.77	13.60
Al30Sb70	84.13	3.94	12.07	70.84	3.26	26.50
Al20Sb80	81.15	0	18.85	35.62	0.88	63.50

Table 4.7. Rietveld refinement calculation comparison of Al – Sb alloy before and after lithiated for 100 cycles.

From the battery performance results, the Al80Sb20 samples exhibited poor electrochemical performance compared to other melt spun samples. By referring to the XRD and the refinement results before and after lithiation in Table 4.7, after lithiation there are a large increase of Al phase amount in the electrode compared to before lithiation, which is due to the incomplete restructuring of AlSb phase leaving an increased amount of unreacted Al phase.

Large amount of Al phase is not desirable as the diffusion of Li into Al particles is very slow at room temperature, at around $6 \times 10^{-12} \text{ cm}^2/\text{s}$, which is at least two orders of magnitude lower compared to the lithium diffusion coefficient in other lithium alloy phases, making the electrode overcharge easily⁵⁷. Due to the slow kinetics of the lithium diffusion in the structure, not all of the Li ions are able to be extracted from the structure when cycled, thus trapping the lithium ions inside the structure. Furthermore, the formation of Al into LiAl due to the lithium insertion into the structure caused volume change of around 96 %⁸ which can cause electrode cracking and loss of contact with the current collector.

Samples	<i>a</i> Lattice parameter (nm)			Crystallite size (nm)		
	Al	Sb	AlSb	Al	Sb	AlSb
Al80Sb20	0.4053	0.4306	0.6126	65.1	16.6	59.8
Al70Sb30	0.4052	0.4309	0.6125	59.7	16.3	55.7
Al60Sb40	0.4052	0.4310	0.6126	58.6	18.1	58.1
Al50Sb50	0.4049	0.4311	0.6125	60.2	18.7	50.3
Al40Sb60	0.4050	0.4314	0.6125	58.9	25.4	52.6
Al30Sb70	0.4053	0.4315	0.6126	57.0	27.1	55.2
Al20Sb80	0.4053	0.4318	0.6128	54.6	31.2	61.4

Table 4.8. Lattice parameter and crystallite size calculation from the XRD samples after lithiation for 100 cycles.

Table 4.8 shows the lattice parameter and the crystallite size of the melt spun electrode samples after cycled for 100 cycles at 100 mA/g. By comparing with the lattice parameter and crystallite size before lithiation in Table 4.3, we can see that the insertion of lithium has increased the lattice parameter of Al and Sb phase, which indicates that a solid solution of Li in Al phase and Sb phase has formed^{70,71}.

However, after lithiation the lattice parameter of AlSb has decreased compared to before lithiation. This is probably due to the restructuring of AlSb phase during cycling which could result in smaller crystals. As during lithium insertion some of Sb from AlSb phase are extracted out from the structure to form Li_3Sb , the remaining Al and Sb particles could regroup together to reform into smaller AlSb phase.

After lithiation, the crystallite size of Al and Sb has increased compared to before lithiation while the crystallite size of AlSb has decreased significantly from around 90 nm to around 50-60 nm. The reduction of the crystallite size is consistent with the reduction of lattice parameter of AlSb phase. The small crystals of AlSb phase is beneficial to the overall

electrochemical performance as it shortens the lithium ion diffusion path into the structure and improves ionic transport.

In summary, both the Al₄₀Ab₆₀ and Al₅₀Sb₅₀ samples have the best electrochemical performance compared to the rest of the Al – Sb alloy samples. The improved electrochemical performance is due to the well distributed AlSb phase throughout the structure. From the XRD and Rietveld refinement results it is revealed that after lithiation process, the AlSb phase undergoes restructuring and resulted in reduced lattice parameter and crystallite size compared to before lithiation process. The combination of the small size and well distributed AlSb phase is an important factor for the improved electrochemical performance.

The XRD results also indicated that some of the Sb particles did not reform into the original AlSb phase, resulting in an increase in amount of Sb and Al. The increase of Sb and Al phases is not desirable as it can reduce the electrochemical performance of the electrode. The performance of the Al₈₀Sb₂₀ is very poor compared to other melt spun samples due to the high amount of Al in the electrode. Al has slow reaction kinetics with lithium compared to other alloys, which could result in the trappings of lithium in the host sites, reducing battery capacity. A high amount of Sb is also not desirable as lithium insertion into Sb to form Li₃Sb has huge volume change of 200 % which could result in cracking and detachment of the active material from current collector.

Chapter 5

Conclusion and Future Work

5.1. Conclusion

In this thesis, synthesis and characterization of melt spun Al – Sb alloy with composition ratio ranging from Al₂₀Sb₈₀ to Al₈₀Sb₂₀ were carried out. A detailed study on the battery performance for lithium ion battery anodes and the factors affecting the electrochemical performance was carried out.

Melt spinning process has been shown to be an efficient route to fabricate intermetallic alloys with high purity and high scalability. The product of melt spinning process is shown to have smaller particle size and unique morphology compared to the conventional method of casting due to the rapid solidification process.

To evaluate the potential of Al – Sb alloy as anode material replacement for lithium ion batteries, the Al – Sb alloys were tested as anode for lithium ion batteries. Among the composition ratios tested, Al₄₀Sb₆₀ and Al₅₀Sb₅₀ samples were found to have the best electrochemical performance. In addition, results also showed that small particle size, maintaining the integrity of the AlSb phase, and maintaining electrical contact with the electrode current collector were important factors in order to achieve a good electrochemical performance. The breakdown of AlSb phase into individual Al and Sb particles has led to cracking and loss of electrode contact due to the large volume expansion during lithiation process.

The Al – Sb alloy synthesized by melt spinning is shown to have improved capacities and good high rate performances compared to the commercially available graphite anode. The melt spinning process has demonstrated to be able to synthesize alloys with little to no impurities that results in high Coulombic efficiency of the samples. Furthermore, the low cost of Al and Sb precursors coupled with the environmentally friendly and scalable approach in melt spinning process makes this system a promising and attractive application in lithium ion battery electrode.

5.2. Future Work

Based on our study on the morphology and electrochemical performance of the Al – Sb alloy by melt spinning, this system has potential to be an alternative replacement for the commercial graphite anode in lithium ion batteries. It has shown to have superior capacity of around 635 mAh/ g and still maintain 500 mAh/ g after 80 cycles, compared to only 372 mAh/ g in graphite anode. However, research of this system has been rather limited until now, and deeper understanding of the Al – Sb system is needed in order to improve on the electrochemical performance.

Further work is still needed in order to fully understand the behavior and reaction mechanism of AlSb, Al, and Sb phase during lithiation process. It will be of interest on observing how the phases interact with each other during lithiation, the factors that can affect the breakdown and reforming of AlSb phase, and the formation mechanism and structure of Li_xAlSb . Synthesis of a tertiary system by combining Al – Sb alloy with another metallic alloys such as Si, Sn, Mn, or Ge by using melt spinning process will be of interest to study the morphology and electrochemical properties of this ternary system.

References

1. Bruno Scrosati, Jürgen Garche. *J. Power Sources* **2010**, 195, 2419–2430.
2. Jeong, G.; Kim, Y. U.; Kim, H.; Kim, Y. J.; Sohn, H. J. *Energy and Environmental Science* **2011**, 4,(6), 1986-2002.
3. David Linden; Reddy, T. McGraw-Hill Inc.: New York, **1995**.
4. Tarascon, J.-M. & Armand, M. *Nature* **2008**, 451, 652.
5. Tarascon, J.-M. & Armand, M. *Nature* **2001**, 414, 359-367.
6. Palacin, M. R. *Chemical Society Reviews* **2009**, 38, 2565.
7. Obrovac, M. N.; Christensen, L.; Le, D. B.; Dahn, J. R. *Journal of the Electrochemical Society* **2007**, 154, 9.
8. W.-J. Zhang. *J. Power Sources* **2011**, 196, 13–24.
9. Winter, M.; Besenhard, J. O.; Spahr, M. E.; Novak, P. *Advanced Materials* **1998**, 10, (10), 725-763.
10. Winter, M.; Besenhard, J. O., *Electrochimica Acta* **1999**, 45, (1), 31-50.
11. J.W. Kim, J.H. Ryu, K.T. Lee, S.M. Oh. *J. Power Sources* **2005**, 147, 227.
12. D. Fateux, R. Koksang, *J. Appl. Electrochem* **1993**, 23, 1.
13. C. Wang, A.J. Appleby, F.E. Little, *J. Power Sources* **2001**, 93, 174.
14. L.Y. Beaulieu, K.W. Eberman, R.L. Turner, L.J. Krause, J.R. Dahn, *Electrochem. Solid State Lett.* **2001**, 4, A137.
15. A. Ulus, Y. Rosenberg, L. Burstein, E. Peled, *J. Electrochem. Soc.* **2002**, 149, A635.
16. H. Li, X. Huang, L. Chen, *Electrochem. Solid-State Lett.* **1998**, 1, 241.

17. R. Alcantara, F.J. Fernandez-Madrigal, P. Lavela, J.L. Tirado, J.C. Jumas, J. Olivier-Fourcade, *J. Mater. Chem.* **1999**, 9, 2517.
18. M. Stjerndahl, H. Bryngelsson, T. Gustafsson, J.T. Vaughey, M.M. Thackeray, K. Edstrom, *Electrochim. Acta* **2007**, 52, 4947.
19. P. Limthongkul, Y.I. Jang, N.J. Dudney, Y.M. Chiang, *J. Power Sources* **2003**, 604, 119–121.
20. S. Matsuno, M. Noji, T. Kashiwagi, M. Nakayama, M. Wakihara, *J. Phys. Chem. C* **2007**, 111, 7548.
21. H. Lia, X. Huang, L. Chen, G. Zhou, Z. Zhang, D. Yu, Y.J. Mo, N. Pei, *Solid State Ionics* **2000**, 135, 181.
22. U. Kasavajjula, C. Wang, A.J. Appleby, *J. Power Sources* **2007**, 163, 1003.
23. A. Trifonova, M. Wachtler, M.R. Wagner, H. Schroettner, C. Mitterbauer, F. Hofer, K.C. Moller, M. Winter, J.O. Besenhard, *Solid State Ionics* **2004**, 168, 51.
24. H. Li, L. Shi, W. Lu, X. Huang, L. Chen, *J. Electrochem. Soc.* **2001**, 148, A915.
25. J. Yang, M. Winter, J.O. Besenhard, *Solid State Ionics* **1996**, 90, 281.
26. I.A. Courtney, W.R. McKinnon, J.R. Dahn, *J. Electrochem. Soc.* **1999**, 146, 59.
27. K.D. Kepler, J.T. Vaughey, M.M. Thackeray, *J. Power Sources* 1999, 81–82, 383.
28. M.A. Reddy, U.V. Varadaraju, *J. Power Sources* **2006**, 159, 336.
29. S. Yoon, A. Manthiram, *Chem. Mater.* **2009**, 21, 3898.
30. G.J. Jeong, Y.U. Kim, H.J. Sohn, T. Kang, *J. Power Sources* **2001**, 101, 201.
31. T. Li, Y.L. Cao, X.P. Ai, H.X. Yang, *J. Power Sources* **2008**, 184, 473.
32. J. Saint, M. Morcrette, D. Larcher, L. Laffont, S. Beattie, J.P. Peres, D. Talaga, M.Couzi, J.M. Tarascon, *Adv. Funct. Mater.* **2007**, 17, 1765.

33. J. Yang, Y. Takeda, N. Imanishi, O. Yamamoto, *J. Electrochem. Soc.* **1999**, *146*, 4009.
34. C.M. Park, S. Yoon, S.I. Lee, J.H. Kim, J.H. Jung, H.J. Sohn, *J. Electrochem. Soc.* **2007**, *154*, A917.
35. H. Lee, Y. Kim, M. Hong, S. Lee, *J. Power Sources* **2005**, *141*, 159.
36. Q. Si, K. Hanai, N. Imanishi, M. Kubo, A. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources* **2009**, *189*, 761.
37. I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* **1997**, *144*, 2943.
38. N. Ding, J. Xu, Y. Yao, G. Wegner, I. Lieberwirth, C. Chen, *J. Power Sources* **2009**, *192*, 644.
39. C.K. Chan, H. Peng, G. Liu, K. Mcilwrath, X.F. Zhang, R.A. Huggins, Y. Cui, *Nat.Nanotechnol.* **2008**, *3*, 31.
40. L.Y. Beaulieu, D. Larcher, R.A. Dunlap, J.R. Dahn, *J. Electrochem. Soc.* **2000**, *147*, 3206.
41. L. Fransson, E. Nordstrom, K. Edstrom, L. Haggstrom, J.T. Vaughey, M.M. Thackeray, *J. Electrochem. Soc.* **2002**, *149*, A736.
42. L.M.L. Fransson, J.T. Vaughey, R. Benedek, K. Edstrom, J.O. Thomas, M.M. Thackeray, *Electrochem. Commun.* **2001**, *3*, 317.
43. J. Wolfenstine, S. Campos, D. Foster, J. Read, W.K. Behl, *J. Power Sources* **2002**, *109*, 230.
44. C.S. Johnson, J.T. Vaughey, M.M. Thackeray, T. Sarakonsri, S.A. Hackney, L. Fransson, K. Edstrom, J.O. Thomas, *Electrochem. Commun.* **2000**, *2*, 595.
45. W.-J. Zhang, *J. Power Sources* **2011**, *196*, 877–885.
46. R. Benedek, M.M. Thackeray, *J. Power Sources* **2002**, *110*, 406.

47. A. Anani, R.A. Huggins, *J. Power Sources* **1992**, 38, 351.
48. M. Wachtler, M. Winter, J.O. Besenhard, *J. Power Sources* **2002**, 105, 151.
49. Dailly, A.; Ghanbaja, J.; Willmann, P.; Billaud, D. *Electrochimica Acta* **2003**, 48, (8), 977-984
50. Kim, M. G.; Cho, J. *Advanced Functional Materials* **2009**, 19, (10), 1497-1514.
51. Scrosati, B., *Electrochimica Acta* **2000**, 45, (15-16), 2461-2466
52. Zhao, H.; Yin, C.; Guo, H.; He, J.; Qiu, W.; Li, Y., *J. Power Sources* **2007**, 174, (2), 916-920.
53. Stjerndahl, M.; Bryngelsson, H.; Gustafsson, T.; Vaughey, J. T.; Thackeray, M.M.; Edström, K., *Electrochimica Acta* **2007**, 52, (15), 4947-4955.
54. Grugeon, S.; Laruelle, S.; Dupont, L.; Tarascon, J. M. *Solid State Sciences* **2003**, 5, (6), 895-904.
55. M.J. Lindsay *et al.* *J. Power Sources* **2003**, 119–121, 84–87.
56. Z. Chen *et al.* / *Electrochimica Acta* **2009**, 54, 4118–4122.
57. Y. Hamon, T. Brousse, F. Jousse, P. Topart, P. Buvat, D.M. Schleich, *J. Power Sources* **2001**, 97–98, 185.
58. R. Hu *et al.* *J. Power Sources* 2009, 188, 268–273.
59. A. Saito, T. Horiba, Y. Aono. The 36th Battery Symposium in Japan, Abstr. 2B07 **1995**.
60. H. Honda *et al.* / *Materials Research Bulletin* **2003**, 38, 647–656.
61. Ishida, K., Shumya, T., Ohtani, H.: *J. Less-Common Met.* **1988**, 143, 279.
62. M. A. Otooni, *Elements of rapid solidification : fundamentals and applications /* Monde A. Otooni, ed: Berlin ; New York : Springer, **1998**.

63. E. H. Strange and C. A. Pim, U.S Patent. Patent no. 905758, **1908**.
64. R. Pond and R. Maddin, *Trans. Met. Soc., AIME*, **1969**, 245, 2475-2476.
65. H. Libermann and C. Graham, Vol Mag-12, No 6, 1976," *IEEE Transactions on Magnetism*, **1976**, 12, 921- 923.
66. R. K. Gupta and K. F. Auyeung, *Journal of Applied Polymer Science* **2003**, 34, 2469 – 2484.
67. R. C. Budhani, T. C. Goel, and K. L. Chopra, *Bulletin of Materials Science* **1982**, 4, 549-561.
68. S. Fan *et al.* *J. Power Sources* **2012**, 201, 288– 293.
69. Seoung-Bum Son *et al.* *Adv. Energy Mater.* **2012**, 2, 1226–1231.
70. Z.B. Sun *et al.* *J. Power Sources* **2008**, 182, 353–358.
71. Linping Zhang *et al.* *J. Solid State Electrochem* **2012**, 42, 843–850.
72. Linping Zhang *et al.* *J. Solid State Electrochem* **2012**, 16, 2159–2167.
73. S.M. O'Flaherty, R. Murphy, S.V. Hold, M. Cadek, J.N. Coleman, W.J. Blau, *J. Phys. Chem. B* **2003**, 107, 958–964.
74. T. Hasan, V. Scardaci, P. Tan, A.G. Rozhin, W.I. Milne, A.C. Ferrari, *J. Phys. Chem. C* **2007**, 111, 12594–12602.
75. S.D. Bergin, V. Nicolosi, P.V. Streich, S. Giordani, Z. Sun, A.H. Windle, P. Ryan, N.P.P. Niraj, Z.-T.T. Wang, L. Carpenter, W.J. Blau, J.J. Boland, J.P. Hamilton, J.N. Coleman, *Advanced Materials* **2008**, 20, 1876–1881.
76. S. Park, T. Kim, S.M. Oh, *Electrochem. Solid-State Lett.* **2007**, 10, A142–A145.
77. M. Gaberscek, M. Kuzma, J. Jamnik, *Phys. Chem. Chem. Phys.* **2007**, 9, 1815–1820.

- 78. P.A. Johns, M.R. Roberts, Y. Wakizaka, J.H. Sanders, J.R. Owen, *Electrochem. Comm.* **2009**, *11*, 2089–2092.
- 79. A.L. Dalverny, J.S. Filhol, M.L. Doublet, *J. Mat. Chem.* **2011**, *21*, 10134–10142.
- 80. S. Park, T. Kim, S.M. Oh, *Electrochem. Solid-State Lett.* **2007**, *10*, A142–A145.
- 81. J.T. Vaughley *et al.* *J. Power Sources* **2001**, *97 – 98*, 194 – 197.
- 82. I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* **1997**, *144*, 2045–2052.