Investigation of tin and antimony based anodes with enhanced cycle life for sodium-ion batteries

Edison, Eldho

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**NANYANG
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SINGAPORE

**INVESTIGATION OF TIN AND ANTIMONY BASED ANODES
WITH ENHANCED CYCLE LIFE FOR SODIUM-ION
BATTERIES**

ELDHO EDISON

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

INVESTIGATION OF TIN AND ANTIMONY BASED ANODES WITH ENHANCED CYCLE LIFE FOR SODIUM-ION BATTERIES

ELDHO EDISON

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

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MADHAVI SRINIVASAN

Authorship Attribution Statement

This thesis contains material from 6 papers published in the following peer-reviewed journals / from papers accepted at conferences in which I am listed as an author.

Chapter 2 is published as **Edison, E.**; Sreejith, S.; Lim, C. T.; Madhavi, S. Beyond intercalation based sodium-ion batteries: the role of alloying anodes, efficient sodiation mechanisms and recent progress. *Sustainable Energy & Fuels* 2018, 2, 2567-2582, DOI: 10.1039/C8SE00381E.

The contribution of the co-authors are as follows:

- Prof. Madhavi and Dr. Sreejith provided the initial direction to write the review and edited the manuscripts.
- I prepared the manuscript drafts and revised the same after discussions with Prof. Madhavi and Dr. Sreejith.
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The contributions of the co-authors are as follows:

- Prof. Madhavi and Dr. V. Aravindan provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. V. Aravindan and Prof. S. Madhavi.

- I co-designed the study with Prof. Madhavi and Dr. V. Aravindan and performed all the laboratory work at the School of Materials Science and Engineering and analyzed the data.
- All XRD measurements and FESEM imaging were conducted by myself in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr. R. Satish carried out the Raman spectroscopy experiments for the samples.
- Dr. W. C. Ling carried out the HRTEM imaging for the samples.

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The contributions of the co-authors are as follows:

- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. S. Sreejith and Prof. S. Madhavi.
- I performed all the materials synthesis, collected X-ray diffraction patterns and FESEM images, carried out device fabrication, and conducted data evaluation.
- Dr. S. Sreejith provided valuable insights to improve the manuscript drafts.

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The contribution of the co-authors are as follows:

- I performed all the materials synthesis, carried out the phase and morphological evaluations, fabricated the devices and analyzed the data and wrote the manuscript drafts.
- Dr. S. Sreejith, Prof. C. T. Lim and Prof. S. Madhavi provided critical insights and discussions to improve the manuscript.
- Dr. R. Hao carried out the HRTEM imaging for the samples

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The contribution of the co-authors are as follows:

- I performed all the materials synthesis, carried out the phase and morphological evaluations, fabricated the devices and analyzed the data and wrote the manuscript drafts.
- Dr. P. K. Gogoi carried out the STEM imaging for the samples.
- Dr. S. Sreejith, Dr. P. K. Gogoi, Prof. S. J. Pennycook, Prof. C. T. Lim and Prof. S. Madhavi provided critical insights and discussions to improve the manuscript.
- Dr. Y. Zheng carried out the HRTEM imaging for the samples.

31-07-2019

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Date

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ELDHO EDISON

Abstract

Sodium-ion batteries (SIBs) are proposed as a low-cost alternative to the existing lithium-ion batteries (LIBs) in view of the abundance and wide distribution of the sodium reserves. To realize the practical deployment of the SIBs, however, it is crucial to develop high-capacity sodium-storage materials. In this thesis, Sn and Sb based materials have been explored considering their high capacity, low cost, environmental benignity and safety aspects. Various scalable, high-throughput and industrially viable synthetic methodologies including melt-spinning and high-energy ball milling techniques have been employed to synthesize the active materials. The sodium-storage mechanism, structural and morphological evolution and transformations in the active materials were probed. The various strategies adopted in the study could significantly improve the cycle life of the anodes, which is considered as the Achilles' heel of alloying and conversion anodes. Additionally, preliminary full-cell investigations were carried out to gauge the practical implications and utility of the synthesized anode materials for sodium-ion batteries. Various novel synthetic methodologies and scientific and technological findings aiding high energy density sodium-ion batteries based on alloying and conversion anodes were achieved. The novel insights from the study as well as the proposed future works could guide and spawn further research and technological advancements towards the practical deployment of SIBs.

Lay Summary

The ever-rising problems of global warming and environmental pollution call for the deployment of renewable energy resources such as solar, wind and tidal power plants. Sodium-ion batteries are considered as an ideal choice as energy storage device for these renewable resources due to their cost benefits when compared to the conventional lithium-ion batteries. However, to realize the practical implementation of sodium-ion batteries, it is vital to develop novel materials that can deliver high sodium storage capacities for several charge-discharge cycles. In this study, such materials which offer high sodium-storage capacities were explored and their performance was evaluated. Mainly, tin and antimony-based materials were investigated considering their large capacities, low-cost and environmental safety benefits. Practically feasible and industrially scalable synthesis methods were adopted to synthesize these materials. Additionally, the investigation of the sodium storage mechanism of these materials has led to several scientific and technological findings. The novel outcomes of the study can serve as guidelines for future researchers to further advance the field and lead to the realization of sodium-ion batteries for real life applications.

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Abbreviations

EC	Ethylene Carbonate
FEC	Fluoroethylene Carbonate
EDX	Energy Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
LIB	Lithium-ion battery
MS	Melt-Spun
NVP	Sodium Vanadium Phosphate
NVPF	Sodium Vanadium Fluorophosphate
PC	Propylene Carbonate
PXRD	Powder X-ray Diffraction
PVP	Polyvinyl Pyrrolidone
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Solid Electrolyte Interphase
SIB	Sodium-ion Battery
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
Z	Atomic Number

Chapter 1

Introduction

The chapter introduces the need for low-cost sodium-ion batteries as electrochemical energy storage systems to enable the widespread utilization of renewable energy resources. In this regard, the role of alloying and conversion anodes to achieve high energy density sodium-ion batteries is emphasized. The significance and the gaps in the current state of research are identified and the scope and objectives of the thesis are stated. A brief overview of the thesis chapters is provided, and the major findings and outcomes are abridged.

1.1 Background and significance

Climate change and environmental pollution exhort the need for the deployment of clean energy resources. However, the implementation of the sustainable yet intermittent energy sources such as solar, wind and tidal power systems necessitates the development of low-cost and reliable electrochemical energy storage systems.¹⁻⁶ Lithium-ion batteries (LIBs) have been conventionally used to meet these energy storage requirements. Additionally, LIBs are also employed to power electric vehicles and are potential candidates for grid storage applications.^{5, 7} However, recent reports suggest the need for alternative energy storage systems in view of the draining lithium deposits and rising prices of Li-based compounds (**Figure 1-1**).^{8, 9}

In this regard, sodium-ion batteries (SIBs) have received significant attention as a suitable substitute to the LIBs.¹⁰⁻²² Sodium reserves are almost inexhaustible and widely distributed aiding significant cost reduction for SIBs when compared to LIBs.⁹ Moreover, sodium is the second lightest alkali metal after Li with redox potential (2.71 vs. SHE) very close to that of Li. Additionally, the similarity in the industrial fabrication and processing routes for SIBs and LIBs would aid the smoother implementation of SIBs for practical applications. The deployment of SIBs in the energy storage applications are proposed to bring forth cost reductions up to 30%.^{22, 23} This is significant, especially for the widespread deployment of renewable energy resources which would require large-format, low-cost and reliable batteries. Consequently, SIBs hold huge potential as cheap and efficient alternatives to the conventional LIBs.

a

b

Figure 1-1. a, Global lithium resource availability map.⁸ b, Elemental abundance of sodium in the earth's crust.⁹

1.2 Problem statement

While SIBs are low-cost alternatives to the existing LIBs, the lower reduction potential (0.3 V less than Li) invites penalty regarding the energy density. As the energy density is directly proportional to the charge capacity, it is vital to develop materials that have high charge storage capacities to achieve high energy density SIBs. Significant progress has been achieved in the development of cathode materials for SIBs and their performances are even at par with the conventional LIB cathode materials (**Figure 1-2**).⁹ However, graphite, the conventional anode for LIBs is found to be an unsuitable host for Na ions.³ This is attributed to the larger size of the Na ions which are unable to intercalate within the graphitic layers (~ 3.4 Å interlayer distance). Other intercalation-based materials such as hard carbon and various metal oxides have been investigated for SIBs. However, the charge storage capacities of the materials are poor because of the limited sodium-storage sites available in these materials.^{3, 12} In this context, alloying and conversion-based materials that possess large sodium storage capacities are of vital importance as they can deliver much higher gravimetric and volumetric energy densities when compared to the intercalation-based materials.

Figure 1-2. Gravimetric capacity of selected cathode materials for SIBs and the average

voltage vs. Na^+/Na .⁹

Group IV elements namely, Sn, Sb, P, Ge are known to undergo electrochemical alloying reactions with Na in a reversible manner and can attain high sodium-storage capacities when compared to carbon-based materials (**Table 1-1**).¹² However, bare Sn or Sb anodes undergo huge volume changes during the sodiation/desodiation reactions resulting in pulverization and loss of electrical contact, leading to poor cycle life for the battery.²⁴ Because of these challenges, the progress in the development of alloying and conversion anodes for SIBs has remained slow-paced (**Figure 1-3**).¹⁷ Hence investigating the sodiation mechanism of these alloying and conversion anodes is essential to devise strategies to mitigate these challenges and improve the cycle life of sodium-ion batteries.

Table 1-1. High capacity Na-alloying anodes.¹²

Element	Sodiated phase	Average operating voltage (V)	Specific capacity (mAh g^{-1})
Sn	$\text{Na}_{15}\text{Sn}_4$	0.5	847
P	Na_3P	0.4	2596
Sb	Na_3Sb	0.6	660
Ge	NaGe	0.4	369

As evident from the Figure 1-3, it is vital to develop Sn and Sb based alloying and conversion anode materials which offer much higher gravimetric and volumetric capacities than the carbon-based materials. Moreover, it is essential to devise strategies to curb the challenges of this class of alloying anodes that undergo huge volume changes during the charge/discharge processes.

Figure 1-3. Theoretical energy densities of various sodium-ion battery anodes. Energy density of commercialized LIBs is represented by the yellow region.¹⁷

1.3 Objectives and Scope

The primary aim of this thesis is to develop anode materials for sodium-ion batteries with high capacity when compared to carbon-based anodes and reliable cycling life to meet practical applications. Hence, with an emphasis on low-cost and practical usability, Sn and Sb-based alloying and conversion- sodium-ion battery anodes possessing the following characteristics will be focused upon:

- Possess high sodium storage capacity leading to high energy density
- Composed of low-cost, environmentally benign materials that could be handled and processed in a large scale
- Maintain good structural integrity during the repeated charge/discharge processes to ensure good battery life
- Excellent electronic and ionic conductivities to achieve good electrochemical performance at high current rates

The above-mentioned aims could be achieved with the following scope and objectives:

1. Investigating the carbon matrix induced performance of Sn-rich FeSn₂ alloy anodes for sodium-ion battery

- Improve the cycle life of bare tin anode by employing Fe as inactive matrix through the synthesis of Sn-rich FeSn₂ alloy anode via facile solvothermal technique.
- Study the electrochemical performance and sodium-storage mechanism of this alloy as sodium-ion battery anode in half-cell configuration.
- Employ high-energy ball milling technique to fabricate FeSn₂/carbon composites and study the electrochemical performance.
- Investigate the effect of commercially available graphite, graphene and Super-P carbon as buffer matrix to improve cycle life.

2. Synthesis of Sb-rich Fe-Sb alloy ribbons via melt-spinning process: investigation and performance evaluation as anodes for sodium-ion battery

- Synthesize Sb-rich Fe-Sb alloy via high-throughput melt-spinning process to improve the cycle life of bare antimony anode.
- Investigate the structural and morphological features of the melt-spun ribbons.
- Study the sodium-storage mechanism and the electrochemical performance in sodium-ion half-cell configuration.
- Investigate practical feasibility of the alloy anode by studying full-cell performance.

3. Melt-spun ternary Fe-Sn-Sb alloys: tuning the microstructure to enhance the cycling stability for sodium-ion battery

- Synthesize SnSb alloy via melt-spinning process and investigate the electrochemical performance in half-cell sodium-ion battery configuration.
- Study the effect of Fe as a buffer matrix to mitigate the stresses associated with the sodiation/desodiation reactions by fabricating Fe-Sn-Sb alloy ribbons.
- Investigate the structural and morphological evolution of the ternary alloy anode during the sodiation/desodiation reactions.
- Fabricate high energy density sodium-ion full-cell by employing a high voltage

fluorophosphate, NaVPO_4F cathode.

4. Design and synthesis of FeSbO_4 nanoparticles: investigating sodium storage pathways and electrochemical performance for sodium-ion battery

- Design a facile and scalable synthetic protocol for FeSbO_4 nanoparticles.
- Study the structural and morphological features of the synthesized FeSbO_4 nanoparticles.
- Investigate the conversion/alloying sodium-storage mechanism and performance in half-cell sodium-ion battery configurations.
- Explore the structural and morphological evolution of the FeSbO_4 anode during sodiation/desodiation reactions.
- Assess the suitability of the conversion anode for practical applications by investigating a full-cell sodium-ion battery.

1.4 Dissertation Overview

The thesis addresses the fundamental challenge of cycling instability in tin and antimony-based alloying and conversion anodes and their implication as high capacity anodes for sodium-ion batteries.

Chapter 1 introduces the background and significance of sodium-ion batteries and exhorts the need for alloying and conversion-based anodes for sodium-ion batteries. Furthermore, the challenges and issues to be addressed for alloying and conversion anodes are discussed and the advantages of tin and antimony-based materials are discussed. Additionally, the objectives and scope of the thesis are laid out, and an overview of the thesis is provided.

Chapter 2 reviews the literature on alloying and conversion anodes for sodium-ion batteries and identifies the gaps in the research field that shaped the objectives of the thesis. The working principle of sodium-ion batteries is explained and the research progress in anodes for sodium-ion batteries are reviewed. The necessity of high capacity anodes is highlighted and tin and antimony-based alloying and conversion anode materials for sodium-ion batteries are reviewed in detail. Additionally, the strategies to mitigate the challenges of

alloying and conversion anodes are identified from literature.

Chapter 3 describes the synthesis methodology adopted, and the characterization techniques utilized in this study both from the material and the device standpoint. The principle and application of various synthesis techniques and characterization tools are detailed. Additionally, the fabrication protocol for sodium-ion batteries and the device characterization techniques are described.

Chapter 4 focuses on tin-based FeSn_2 anode and investigates the electrochemical performance in sodium-ion batteries. The synthesis and characterization of highly phase-pure nanostructured FeSn_2 particles is described. The electrochemical performance of FeSn_2 anode in sodium-ion batteries is investigated. The influence of carbon matrix to enhance the cycling stability is explored in depth.

Chapter 5 focuses on antimony-based Fe-Sb anode for sodium-ion batteries. It details a high-throughput melt-spinning process for the synthesis of the alloy ribbons. The structural and morphological characterization of the alloy ribbons is described. The electrochemical performance and sodium-storage mechanism is investigated. Moreover, preliminary full-cell sodium-ion battery investigations to gauge the practical feasibility of the alloy anode are described.

Chapter 6 investigates ternary Fe-Sn-Sb alloy anode performance for sodium-ion batteries. The cycling stability of bare SnSb and Fe-Sn-Sb ternary anodes are investigated. The structural and morphological evolution of the ternary anode during sodiation/desodiation reactions are investigated. The sodiation mechanism of the ternary anode is investigated and the enhancement of cycling stability is explored. Moreover, a high energy density sodium-ion full cell based on the ternary alloy anode and a fluorophosphate cathode is described.

Chapter 7 explores the design and synthesis of novel alloying-conversion anode FeSbO_4 for sodium-ion batteries. The synthetic route for highly phase pure FeSbO_4 nanoparticles

is designed and the material is characterized. The sodiation mechanism and the morphological evolution are explored in detail by operando and ex situ investigations. Additionally, the full-cell performance is gauged by coupling with a fluorophosphate cathode.

Chapter 8 concludes the study and summarizes the major findings and novel contributions of the study. Additionally, future work recommendations that could help advance the field of alloying and conversion anodes for sodium-ion batteries are also discussed.

1.5 Findings and Outcomes

The novelties of the study could be identified as follows:

- Optimized the carbon matrix for alloy-carbon composites to enhance the cycle life of sodium-ion battery anodes. The study could develop FeSn₂/Graphite anode offering enhanced cycle life via high throughput ball milling technique.
- Developed Fe-Sb anode via industrially viable melt-spinning process. Revealed the phase transformations and sodiation mechanism of the alloy ribbons. Obtained enhanced performance in half-cell and full-cell configurations.
- Synthesized novel Fe-Sn-Sb ternary alloy anodes for sodium-ion batteries. Elucidated the sodiation mechanism and the structural/morphological evolution in the anode. Fabricated FeSnSb/NVPF high energy density full-cell with excellent electrochemical performance.
- Designed synthesis route to obtain FeSbO₄ nanoparticles. Revealed the electrochemically induced amorphization in FeSbO₄ during sodium storage. Unveiled the sodium-storage mechanism and phase transformations in FeSbO₄ anode during sodium storage. Designed a FeSbO₄/NVPF full-cell offering high energy density.

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Chapter 2

Literature Review

In this chapter, the construction and working of sodium-ion batteries (SIBs) are introduced, and the potential cost benefits and applications are highlighted. The research progress on anodes for sodium-ion batteries is summarized. The need for high capacity alloying and conversion anodes to enable high energy-density SIBs is emphasized and the challenges accompanying their successful implementation are reviewed. Moreover, the sodiation mechanism of tin and antimony anodes as well as the recent progress in the field are summarized. Additionally, various strategies to mitigate the challenges of employing high capacity alloying and conversion anodes are discussed.

2.1 Overview of Sodium-ion batteries

Sodium-ion batteries (SIBs) are proposed as a viable alternative to the conventional lithium-ion batteries (LIBs), especially for large-format, low-cost applications. As opposed to LIBs, SIBs rely on the widely distributed and nearly 1000 times more abundant sodium reserves which could lead to nearly 30% reduction in costs.¹ The configuration and working of SIBs is very much like that of the conventional LIBs (**Figure 2-1**).² The SIB consists of an anode, a cathode and a separator, all of which are immersed in an electrolyte solution. When the battery is charged by the power supply, sodium-ions are removed from the cathode and intercalate into the anode while electrons travel from the cathode to the anode through the external circuit and maintains the charge neutrality. During discharge, the sodium-ions shuttle back from the anode to the cathode while electrons travel through the external circuit powering the load.²

Figure 2-1. Configuration and working of a sodium-ion battery.²

2.2 Research progress on anodes for sodium-ion batteries

Learning from the exhaustive research on LIBs, there has been rapid progress in the

materials explored as sodium-ion battery anodes. Among others, oxides³⁻⁵, carbon-based materials⁶⁻¹⁰, sulfides¹¹⁻¹³ have been explored as anodes as seen from Figure 2-2. While graphite, the conventional anode for LIB is found to be unsuitable to intercalate Na ions, hard carbon has been widely explored as Na-ion host.^{6, 9, 14-16} However, the low tap density of hard carbon leads to poor gravimetric and volumetric energy densities. Evidently, the volumetric and gravimetric capacities of SIBs can be increased by making use of alloying and conversion-based anode materials.

Figure 2-2. Theoretical capacities of various anode materials for SIBs.¹⁷

2.3 Tin-based anode materials for sodium-ion batteries

Tin (Sn) is known to electrochemically alloy with Na and upon full sodiation, the $\text{Na}_{15}\text{Sn}_4$ phase formed corresponds to a capacity of 847 mAh g^{-1} .^{18, 19} Additionally, tin is one of the cheapest and abundant elements as well as non-toxic, making it an ideal anode material for sodium-ion batteries. Various groups have explored the sodiation/desodiation mechanism of Sn anode for SIBs. Among others, Chevrier *et al.*²⁰ calculated the theoretical voltage profile for the Na-Sn system and proposed the sodiation of Sn via several intermediates such as NaSn_5 , NaSn , Na_9Sn_4 terminating in $\text{Na}_{15}\text{Sn}_4$ (Figure 2-3a). Recently, Stratford and

group²¹ predicted various Na-Sn structures by employing *ab initio* random structure searching and screening from the structural database. By making use of *operando* XRD analysis coupled with pair distribution function (PDF) investigations, the local and long range structural investigations revealed the following mechanism (Figure 2-3c):

Step 1: $\text{Sn} \rightarrow \text{NaSn}_3$

Step 1': $\text{Sn}, \text{NaSn}_3 \rightarrow \text{NaSn}_2$

Step 2: $\text{NaSn}_2 \rightarrow \text{a-Na}_{1.2}\text{Sn}$

Step 2': $\text{a-Na}_{1.2}\text{Sn} + \text{NaSn}_2 \rightarrow \text{a-Na}_{1.2}\text{Sn} + \text{expanded Na}_{1+x}\text{Sn}_2 \text{ (solid solution)}$

Step 3: $\text{a-Na}_{1.2}\text{Sn} + \text{expanded Na}_{1+x}\text{Sn}_2 \rightarrow \text{Na}_{4.4}\text{Sn}_2$

Step 3': $\text{Na}_{4.4}\text{Sn}_2 \rightarrow \text{Na}_{4.75}\text{Sn}_2 \text{ (solid solution)}$

Step 4: $\text{Na}_{4.75}\text{Sn}_2 \rightarrow \text{Na}_{15}\text{Sn}_4$

Step 4': $\text{Na}_{15}\text{Sn}_4 \rightarrow \text{Na}_{15+x}\text{Sn}_4$

a: amorphous

During the initial sodiation of Sn, a layered structure of approximate stoichiometry Na_3Sn forms and subsequently NaSn_2 is formed which is thermodynamically stable and structurally like NaSn_3 . A crystalline to amorphous transformation was observed upon further sodiation. The amorphous phase was found to contain chains of Sn atoms with an approximate composition of $\text{Na}_{1.2}\text{Sn}$ and further sodiation led to Sn-Sn dumbbell structures through a solid-solution mechanism. This process culminated in the formation of $\text{Na}_{44.75}\text{Sn}_2$. *Ex situ* PDF measurements confirmed the formation of $\text{Na}_{15}\text{Sn}_4$ upon full sodiation reaction. Moreover, the NMR measurements led to the proposition of excess sodium incorporation

to form $\text{Na}_{15+x}\text{Sn}_4$ as it would not require any Sn-Sn bond breaking.

Figure 2-3. (a) Sodioted phases of tin. (b) Formation enthalpy per atom vs. sodium concentration in the Na–Sn compound and electrochemistry data of the sodium–tin cell cycled at a rate of $C/20$ (corresponding to achieving a capacity of 847 mA h g^{-1} in 20 h) between 2 and 0.001 V (black line). (c) *Operando* measurements of tin vs. sodium showing selected PDFs and ^{23}Na -NMR spectra, and the corresponding potential profile obtained during the first discharge.²² (Reproduced with permission of The Royal Society of Chemistry).

However, bare Sn anode undergoes huge volume expansion (~420%) upon the sodiation reaction and repeated charge/discharge cycles lead to pulverization and loss of electrical contact. This leads to poor cycling stability of bare Sn anode-making it practically unsuitable despite its high capacity. Various strategies including structural modifications and incorporation of active/inactive buffer matrix have been adopted to improve the cycling stability of Sn-based anodes and are summarized in Table 2-1.

Table 2-1. Sn-based anodes-comparison of electrochemical performance

Sn-based anodes-morphology/structure	Synthesis method	Sodiation capacity (second cycle)	Capacity retention (cycle life)	Potential Window (V vs. Na)
Porous tin ²³	Phase-inversion technique	659 mAh g ⁻¹ @423.5 mA g ⁻¹	~77% (500 cycles)	0.001-1
Tin nanoparticles encapsulated in graphene backboned carbonaceous foams ²⁴	Hydrogen-assisted thermal reduction	~600 mAh g ⁻¹ @400 mA g ⁻¹	~84% (500 cycles)	0.01-2
Sn nanoparticles@nitrogen-doped carbon nanofiber composites ²⁵	Electrospinning	~690 mAh g ⁻¹ @84.7 mA g ⁻¹	~87% (200 cycles)	0-2.5
Sn coated reduced graphene oxide-graphene composite ²⁶	Camera flash reduction	~690 mAh g ⁻¹ @423.5 mA g ⁻¹	~72% (100 cycles)	0.01-2
Yolk-shell carbon encapsulated tin ²⁷	Hydrothermal synthesis	~500 mAh g ⁻¹ @100 mA g ⁻¹	~80% (100 cycles)	0.02-3
Multi-layered 2D Sn Nano-dendrites ²⁸	Electrodeposition	~783 mAh g ⁻¹ @100 mA g ⁻¹	~96% (300 cycles)	0.001-0.65
Sn ₄ P ₃ nanotops ²⁹	Solution-based synthesis	~600 mAh g ⁻¹ @50 mA g ⁻¹	~83% (80 cycles)	0.01-2
Sn ₄ P ₃ /Reduced graphene oxide hybrids ³⁰	Solution-based synthesis	~900 mAh g ⁻¹ @100 mA g ⁻¹	~77% (100 cycles)	0.01-3
Sn ₄ P ₃ /Graphene nanocomposite ³¹	Mechanochemical synthesis	~600 mAh g ⁻¹ @1 A g ⁻¹	~99% (1000 cycles)	0-2
Intermetallics of Sn				
SnTe-carbon composite ³²	Solid state synthesis	~541 mAh g ⁻¹ @50 mA g ⁻¹	~99.1% (100 cycles)	0-2.5
MnSn ₂ alloy ³³	Ball milling method	~400 mAh g ⁻¹ @18.35 mA g ⁻¹	~89.8% (50 cycles)	0-1.5
SnSe Nanoparticles Confined in Graphene ³⁴	Ball milling method	~410 mAh g ⁻¹ @1 A g ⁻¹	~95% (120 cycles)	0.01-2
SnSe ₂ 2D Anodes ³⁵	Hydrothermal method	~600 mAh g ⁻¹ @100 mA g ⁻¹	~88% (100 cycles)	0.005-2.5
SnCo/carbon composite ³⁶	Solution-based synthesis	~300 mAh g ⁻¹ @100 mA g ⁻¹	~87% (120 cycles)	0.1-2

2.4 Antimony-based anodes for sodium-ion batteries

Antimony (Sb) is another promising alloying anode for SIBs and it offers a high theoretical capacity of 660 mAh g⁻¹ by forming Na₃Sb upon full sodiation. The sodiation mechanism of Sb has been explored by various groups. Among others, Baggetto *et al.* employed ¹²¹Sb Mossbauer spectroscopy to investigate sodiation of thin films of Sb. An amorphous NaSb intermediate was observed prior to the formation of Na₃Sb upon full sodiation. Later studies from Monconduit *et al.* on micrometric Sb suggested the buffering of the volumetric strains by an amorphous intermediate leading to improved sodiation performance. Recently, Allan *et al.* investigated the sodiation mechanism of Sb by means of solid-state NMR and PDF analysis. The sodiation/desodiation mechanism was revealed, unveiling the previously unknown intermediates (Figure 2-4):

1st sodiation: c-Sb → a-Na_{3-x}Sb + c-Na₃Sb → c-Na₃Sb

1st desodiation: c-Na₃Sb → a-Na_{1.7}Sb → a-Na_{1.0}Sb → a-Na_{1.0}Sb + c-Sb

2nd sodiation: a-Na_{1.0}Sb + c-Sb → a-Na_{1.7}Sb + c-Sb → a-Na_{1.7}Sb + a-Na_{3-x}Sb → a-Na_{3-x}Sb
→ c-Na₃Sb

c: crystalline, a: amorphous.

The sodiation of Sb was found to proceed sequentially at different voltages and involved the formation of two amorphous phases Na_{3-x}Sb and Na_{1.7}Sb. As a result of the sequential sodiation process, the inactive component buffered the stress generated during the sodiation of the active components and upon full sodiation, both crystalline and amorphous antimony networks were observed in the electrode. The formation of crystalline Na₃Sb phase aided facile structural transformation leading to high sodium mobility and consequently good rate performance.

Figure 2-4. (a) Structural changes to antimony during the sodiation/de-sodiation process. (b) PDF and NMR derived mechanisms of (de) sodiation of antimony. (c) (De)sodiation curves and corresponding dQ/dV plots for the 1st and 2nd cycles at a C/20 rate.²² (Reproduced with permission of The Royal Society of Chemistry).

However, sodiation of Sb to form Na₃Sb is accompanied by huge volume changes of ~293%. This leads to particle pulverization and the freshly formed Sb surfaces form new solid electrolyte interphase (SEI) layers causing irreversible capacity losses. Some of the strategies adopted to tackle these issues are summarized in Table 2-2.

Table 2-2. Recent developments in Sb-based anodes for sodium-ion batteries

Sb-based anodes-morphology/structure	Synthesis method	Sodiation capacity (second cycle)	Capacity retention (cycle life)	Potential window (V vs. Na)
Antimony Hollow Nanospheres ³⁷	Galvanic replacement reaction	~627 mAh g ⁻¹ @ 400 mA g ⁻¹	~99.6% (50 cycles)	0.01-2
Cypress leaf-like Sb ³⁸	Chemical replacement reaction	~640 mAh g ⁻¹ @ 100 mA g ⁻¹	~98% (120 cycles)	0.01-2
Sb nanoparticles anchored on carbon nanofibers networks ³⁹	Pyrolysis combined with NaBH ₄ reduction	~542 mAh g ⁻¹ @ 100 mA g ⁻¹	~96.7% (100 cycles)	0.01-2
3-D gradational Sb-NiSb-Ni heterostructures ⁴⁰	Pulsed electrodeposition	650 mAh g ⁻¹ @ 66 mA g ⁻¹	~62% (300 cycles)	0.01-1.5
Spherical nano Sb-carbon composite ⁴¹	Spray pyrolysis	~435 mAh g ⁻¹ @ 100 mA g ⁻¹	~88.5% (500 cycles)	0.01-2
Sb Nanospheres on Graphene ⁴²	Solution-based synthesis	~460 mAh g ⁻¹ @ 250 mA g ⁻¹	~97% (200 cycles)	0.01-2
Sb/C Fibers ⁴³	Electrospinning	~420 mAh g ⁻¹ @ 100 mA g ⁻¹	~83% (300 cycles)	0-2
Sb nanodots embedded 2D carbon nanosheets ⁴⁴	Solution-based top-down strategy	~461 mAh g ⁻¹ @ 100 mA g ⁻¹	~82% (250 cycles)	0.005-2
Intermetallics of Sb				
SnSb nanocrystals ⁴⁵	One-pot reduction	~400 mAh g ⁻¹ @ 660 mA g ⁻¹	~87% (100 cycles)	0.02-1.5
Reduced Graphene Oxide/SnSb nanocomposites ⁴⁶	Hydrothermal reaction	~450 mAh g ⁻¹ @ 100 mA g ⁻¹	~87% (80 cycles)	0.001-2.5
Nanoporous Bi ₂ Sb ₆ ⁴⁷	Chemical dealloying process	~562 mAh g ⁻¹ @ 200 mA g ⁻¹	~76% (100 cycles)	0.01-2
Cu ₂ Sb Nanoparticles integrated on Cu Foil ⁴⁸	Replacement reaction	~400 mAh g ⁻¹ @ 660 mA g ⁻¹	~98% (200 cycles)	0.05-2
Ni-Sb intermetallic hollow nanospheres ⁴⁹	Solvothermal and ball milling method	~600 mAh g ⁻¹ @ 66 mA g ⁻¹	~83% (70 cycles)	0.01-2
Zn ₄ Sb ₃ intermetallic nanowires ⁵⁰	Self-catalysis using reactive vapor transport	~350 mAh g ⁻¹ @ 41.4 mA g ⁻¹	~86% (200 cycles)	0.01-2
Zn ₄ Sb ₃ Films ⁵¹	Electrodeposition	~400 mAh g ⁻¹ @ 97.2 mA g ⁻¹	~90% (250 cycles)	0.1-1.2

2.5 Conversion anodes for sodium-ion batteries

Conversion anodes are characterized by the multiple electron transfer reactions delivering high theoretical specific capacity. Generally, transition metal compounds of the formula M_aX_b where M =transition metal and X = H, F, O, S, N, P, etc., undergo conversion reactions delivering high sodium storage capacities. Additionally, various tin and antimony-based oxides and sulfides have also been explored as conversion anodes. During the conversion reaction, the active material reduces into metallic nanoparticles embedded in Na_2O matrix. By making use of transition metal compounds with the metal involved at its highest oxidation state, the specific capacity of the electrode could be increased. However, similar to alloying anodes, the conversion anodes are also affected by the large volume changes as well as the electrolyte decomposition issues. Various transition metal oxides, sulfides, nitrides and phosphides have been recently explored as viable anodes for sodium-ion batteries and are summarized in Table2-3.

Figure 2-5. Metal oxides and sulfides exhibiting high sodium storage capacities.¹¹

Table 2-3. Recent developments in conversion anodes for sodium-ion batteries

Morphology/ structure	Synthesis method	Sodiation capacity (second cycle)	Capacity retention (cycle life)	Potential window (V vs. Na)
SnO ₂ /rGO ⁵²	Hydrothermal reaction	330 mAh g ⁻¹ @ 100 mA g ⁻¹	~81.3% (150 cycles)	0.005-2.5
SnO ₂ @C hollow nanostructure ⁵³	Template assisted synthesis	200 mAh g ⁻¹ @ 4.6 A g ⁻¹	~90% (3000 cycles)	0.005-2.5
Amorphous SnO ₂ /graphene aerogel ⁵⁴	Hydrothermal reaction	380.2 mAh g ⁻¹ @ 50 mA g ⁻¹	~91.7% (100 cycles)	0.01-3
SnO ₂ /CNT ⁵⁵	Hydrothermal reaction	630.4 mAh g ⁻¹ @ 100 mA g ⁻¹	~79% (100 cycles)	0.005-3
SnS ₂ /rGO ⁵⁶	Hydrothermal reaction	500 mAh g ⁻¹ @ 1 A g ⁻¹	~90% (400 cycles)	0.01-2.5
Sb ₂ O ₃ thin film ⁵⁷	Electrostatic spray deposition	450 mAh g ⁻¹ @ 500 mA g ⁻¹	~92% (200 cycles)	0.01-2
Sb ₂ O ₃ /rGO ⁵⁸	Microwave- assisted synthesis	546 mAh g ⁻¹ @ 100 mA g ⁻¹	~92% (50 cycles)	0.005-3
Sb ₂ S ₃ nanorods ⁵⁹	Hydrothermal reaction	~800 mAh g ⁻¹ @ 100 mA g ⁻¹	~71% (100 cycles)	0-2
MoS ₂ /Graphene composite paper ⁶⁰	Vacuum filtration	~338 mAh g ⁻¹ @ 25 mA g ⁻¹	~83% (20 cycles)	0.1-2.25
WS ₂ nanowires ⁶¹	Solvothermal reaction	~605.3 mAh g ⁻¹ @ 100 mA g ⁻¹	~80% (50 cycles)	0.5-3
TiO ₂ (B) particles ⁶²	Solution-based synthesis	~150 mAh g ⁻¹ @ 15 mA g ⁻¹	~66% (75 cycles)	0.1-2

In short, Na intercalation materials still suffer from limited capacity utilization due to their intrinsic constraint ascribed to their structures, which lowers the specific energy density of SIBs. On the other hand, alloying and conversion materials can be suggested as attractive anodes for SIBs because they can store a large number of sodium ions in the host structure with a relatively low operating potential (below 1.0 V). Multiple reactions with Na per single atom produce a high specific capacity during the alloying–dealloying reactions. Ideal alloying and conversion materials needs to be engineered to curb the challenges of volume expansion, particle pulverization and capacity fading, in order to make them viable for practical applications.⁶³

2.6 Strategies to mitigate the poor cycling stability of alloying and conversion anodes

To deploy alloying anodes for practical applications, it is crucial to tackle the problem of poor cycling stability due to the large volume expansion during the alloying reaction with sodium. Some of the strategies adopted to improve the cycling stability can be summarized as follows:

2.6.1 Tuning the active materials

The problem of particle pulverization and detachment from the current collector could be significantly alleviated by the structural and morphological modifications to the active material in the electrode. Various research groups have found that making the active materials porous/hollow would improve the cycling life. However, the synthesis of porous active materials at a large scale seems to be cumbersome and unfeasible. Another approach was to employ carbon matrix for the active material which would buffer the volume changes occurring during the sodiation/desodiation reactions. Moreover, the carbon matrix improves the conductivity of the electrode as well, leading to enhanced rate performances. Additionally, nano-engineering the active material could also improve the cycling stability as nanomaterials are known to withstand the stresses and strains better than their bulk counterparts.

2.6.2 Incorporating active/inactive components in the electrode

To improve the cycling performance of bare Sn or Sb, intermetallic M-Sn or M-Sb could be employed where M is electrochemically active or inactive. During the initial sodiation of the intermetallic anode, the component M is extracted and acts as a buffer for the sodiated active component Sn or Sb. For instance, in the case of FeSn₂, Fe forms a conductive buffering matrix facilitating the sodiation of Sn. In the case of SnSb, both Sn and Sb are electrochemically active and the sequential sodiation of Sn and Sb buffers the volume changes in the electrode.

2.6.3 Stable solid-electrolyte interphase (SEI) layer

The stability of the SEI layer is an important factor determining the cycling stability of alloying and conversion anodes. When the active materials undergo pulverization, the freshly formed surfaces are exposed to the electrolyte and new SEI layers are formed leading to irreversible capacity losses. The widely used electrolyte for sodium ion battery research is NaClO₄ salt in propylene carbonate/ethylene carbonate-based solvents. The use of fluoroethylene carbonate as additive has been found to improve the cycling stability of alloying and conversion anodes. This has been attributed to the formation of a stable SEI interphase facilitating enhanced electrochemical performance.

2.6.4 Ideal choice of binder for electrode fabrication

The choice of suitable binder during the electrode fabrication process can curb the ill-effects of huge volume expansion. Cross-linked chitosan-based binders and carboxymethyl cellulose binders have been reported to possess excellent mechanical stability thereby improving the cycling life. Moreover, the use of water as the solvent for these cellulose-based binders can help replace use of toxic solvents such as NMP.

2.7 Conclusion

To summarize, sodium-ion batteries are proposed as cost-effective alternatives to the lithium-ion batteries for applications requiring large-format low-cost batteries, including grid storage and electric vehicles. The literature on sodium-ion batteries assert the need for developing materials with high gravimetric and volumetric energy densities for sodium-ion batteries. Earth abundant, non-toxic and cost-effective tin and antimony-based alloying and conversion materials are potential candidates in this regard and various strategies need to be adopted to mitigate the challenges and realize their potential implementation for real-life applications. The objectives and aims of this thesis have been formulated and aligned to investigate and mitigate these challenges.

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Chapter 3

Experimental Methodology

This chapter elucidates the principles and applications of various synthesis and characterization techniques and device fabrication methods adopted in this study. Various synthesis techniques that were adopted to produce the active materials for sodium-ion batteries are discussed in the first section. The principles and the applications of these synthesis techniques are highlighted. The second section elaborates on the characterization techniques employed in the study including the ones used to identify the phases, the structural and morphological features of the synthesized materials. These techniques include X-ray diffraction, microscopy and spectroscopy techniques, among others. Finally, the scheme to fabricate the sodium-ion battery device and the testing protocols adopted to evaluate its electrochemical performances are expounded in the final section.

3.1 Synthesis

3.1.1 Hydrothermal and solvothermal syntheses

Hydrothermal and solvothermal techniques are widely used for the synthesis of diverse inorganic functional materials, nano and ultrafine powders and single crystals. Hydrothermal synthesis refers to the synthetic process carried out via chemical reactions in an aqueous solution above the boiling point of water while solvothermal synthesis makes use of a non-aqueous solution at elevated temperatures.¹

3.1.1.1 Principle

The key features of the hydrothermal and the solvothermal reaction systems are the non-ideal and the non-equilibrium states. Under the high temperature and pressure conditions, water or other solvents can be activated. Powders or single crystals can be synthesized by chemical reaction of multicomponent reactants. For example:

Hydrothermal and solvothermal synthesis can be classified into subcritical and supercritical synthesis reactions depending on the reaction temperature employed. For the subcritical synthesis reaction, the temperature in the range of 100-240 °C is employed and is industrially viable and feasible for laboratory operations. For instance, the synthesis of zeolites falls under the subcritical regime. In the case of supercritical synthesis, high temperatures of ~1000 °C and pressures of the order of 0.3 GPa could be reached.

Figure 3-1. a) Temperature-density plots of water with pressure as a parameter. b) P-T correlation for water with the filling factor of the sealed reactor as a parameter.¹

The density, viscosity and surface tension of water will be lower at high temperature and pressure conditions while the vapor pressure and ion product will be higher (Figure 3-1a).¹ Additionally, the degree of fill of the reaction solvent also influences the prevailing pressure under the hydrothermal conditions (Figure 3-1b). The hydrothermal process involves the following features: a) acceleration of the reaction rate among the complex ions; b) intensifying the hydrolyzation reaction; c) greatly altering the redox potential of the reactants. In summary, under high temperature and pressure conditions, water may act as a solvent or a part of the reactants in some cases, accelerate the reaction by changing the chemical and physical properties of the reactants and products and transfer pressure.

3.1.1.2 Applications

In this work, solvothermal synthesis was employed making use of Teflon-lined 45 ml autoclaves from Parr. The temperature conditions were set in a BINDER oven to carry out the reaction. This technique was employed for synthesis of nanostructured FeSn₂ alloy powders of high crystallinity and phase purity.

3.1.2 High-energy ball milling

High-energy ball milling was developed at the International Nickel Company in the late of 1960. The method proved useful as an alternative to the conventional powder metallurgy methods to produce fine, uniform dispersions of oxide powders such as Al_2O_3 , Y_2O_3 , ThO_2 . The high-energy ball milling technique could also replace some of the high-temperature synthesis processes.²⁻⁴

3.1.2.1 Principle

Figure 3-2. Schematic representation of the ball milling process.⁵

The high-energy ball milling process requires a milling bowl filled with powder and set of balls (Figure 3-2). During the milling process, the powder particles encounter high energetic impact. Initially, because of the compressive forces due to the collision of balls, the powder particles are flattened. The powder particles undergo deformation and changes in the shape because of the repeated impact by the milling balls. After a while, fracture and cold-welding processes occur, and diffusion distances reduce to the micrometer range. At the final stage, the powder particles become extremely deformed and alloying reactions reach completion.

3.1.2.2 Applications

SPEX 8000D Mixer/Mill was used in this work for high-energy ball milling. It consists of a pair of stainless steel vials with stainless steel ball set. The powder is filled in the vials and the vibratory mill swings the vials back and forth during the ball milling process. The balls to sample weight ratio used was 10:1. Additionally, the powders were sealed in the vials in an Ar glovebox to prevent any oxidation during the milling process. In this work, the method was adopted in the synthesis of FeSn₂/Graphite composites.

3.1.3 Melt-spinning or rapid solidification synthesis

Melt-spinning is an industrially viable technique to produce thin flakes/ribbons of amorphous metal alloys by ultrafast cooling of the melt on the surface of a rotating wheel. The technique has been employed to form nanostructures by controlled crystallization to improve the mechanical and magnetic properties of the alloy.^{6, 7}

3.1.3.1 Principle

Figure 3-3. Melt-spinning setup used for the synthesis of rapidly solidified ribbons.⁸

The melt-spinning process is schematically illustrated in Figure 3-3. The starting metal powders are initially cold pressed to a pellet. The pellet is then fed into a quartz crucible with a slit nozzle. The melt-spinning setup has RF induction coils which can melt the pellet and the pressurized Ar gas forces out the melt through the nozzle slit. The molten alloy

then falls onto the water-cooled rotating copper wheel and solidifies to form ribbons. The high cooling rates ($> 10^6 \text{ K s}^{-1}$) impart nanocrystalline and amorphous microstructures to the alloys formed.

3.1.3.2 Applications

Edmund Buhler GmbH single roller melt-spinner was used in this work. The distance between the quartz nozzle and the copper wheel was set 0.75 mm and the frequency of the rotation was 55 Hz. In this work, melt-spinning was used for fabricating FeSb₂ and Fe-Sn-Sb ternary alloys.

3.1.4 Solid-state synthesis

Solid-state synthesis is perhaps one of the oldest and widely used method to make inorganic solids by mixing together the reactants and heating the mixture in a furnace for a set temperature and duration. The method is widely used for making oxides, alloys and ceramics among others.

3.1.4.1 Principle

Based on the investigations of the phase diagram of the desired product and the precursors, optimal synthesis conditions such as temperature are determined. When the temperature is raised above two thirds of the melting point of the precursors, solid state materials become reactive (Tammann's rule).^{9, 10} The conditions for the solid state reaction are also influenced by the precursor properties including surface area, thermodynamic free energy change and reactivity.¹¹ With the increase in temperature, diffusion of precursors occurs and the desired product is formed accompanied at times by the release of gases.

3.1.4.2 Applications

In this work, solid-state synthesis was carried out using two types of furnaces: (i) Carbolite muffle furnace in an air atmosphere (ii) Carbolite Tube furnace in an inert Ar atmosphere.

The heating parameters include ramp rate ($^{\circ}\text{C}/\text{min}$), dwell time and set temperature of reaction. In this work, solid state synthesis was employed to obtain FeSbO_4 nanoparticles using the Carbolite muffle furnace. The Carbolite Tube furnace was used for synthesis of NaVPO_4F cathode material.

3.2 Material Characterization

3.2.1 X-ray Diffraction (XRD)

X-ray diffraction is one of the most widely used techniques for phase identification of crystalline materials including minerals, metal oxides and alloys. The technique makes use of the interference of X-rays and the crystal lattice which acts as diffraction gratings for the X-rays.

3.2.1.1 Principle

The X-ray diffraction technique is based on the Bragg's law of diffraction¹²:

$$n\lambda = 2d \cdot \sin\theta$$

where,

n is an integer signifying the order of the reflection

λ is the incident X-ray wavelength

d is the inter-planar distance between the lattices

θ is the angle of diffraction

Figure 3-4. Principle of X-ray diffraction.¹³

As depicted in Figure 3-4, when the X-rays are incident on the surface of a crystalline sample, they undergo constructive interference when the Bragg's Law is satisfied. The randomly oriented lattices in the sample undergo constructive interference at diverse angles. The intensities of the diffracted X-rays are counted and processed. As the wavelength of X-ray is known and the d-spacing can be calculated. To identify the phases present in a powder sample, the reference patterns in the crystal structure database are utilized and can be analyzed as each phase has a unique set of d-spacings.

3.2.1.2 Rietveld refinement

The Rietveld refinement technique of XRD patterns is used to refine the experimental XRD patterns of the sample against a theoretical structural model from the database using a least squares algorithm. This is usually carried out using software such as TOPAS. Refinement can yield the phase details as well as the lattice parameters of the phases in the sample. In a multiphase sample, the technique can provide the relative amounts of the phases present.¹⁴

3.2.1.3 Applications

In this work, XRD was widely used for phase analysis of the synthesized samples as well as the samples after sodiation/desodiation reactions. Bruker D8 Advance XRD with CuK α radiation of wavelength 1.5404 Å was used for the XRD studies. The Rietveld refinement of the XRD patterns were carried out in a licensed TOPAS V4 software.

3.2.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is widely used to investigate the morphology and the surface topography of samples. The greater resolution of the electron microscope enables the visualization of nano-sized particles and morphological details.

3.2.2.1 Principle

The sample surface is probed with a beam of electrons and the electron-sample interaction produces signals including secondary electrons and back scattered electrons (Figure 3-5). The secondary electrons are produced by the ionization of the atoms on the sample surface by the electron beam and contain information about the surface topography of the sample. These are detected by a detector carrying some bias and provides a resolution of $\sim 1-2$ nm of the topography.

Figure 3-5. Interaction of electron beam with the sample.¹⁵

The contrast achieved in SEM imaging is by edge-effect (Figure 3-6) as edges are brighter than flat surfaces due to the greater number of electrons released.¹⁶

Figure 3-6. Edge-effect in secondary electron imaging of surface topography.¹⁶

3.2.2.2 Application

The SEM was employed in this work to examine the morphology of the synthesized samples. JEOL FESEM 6340 and 7600F were used in this study.

3.2.3 Energy Dispersive X-ray Spectroscopy (EDX)

The EDX technique is employed to characterize the elemental distribution in a sample by making use of the characteristic X-rays emitted when irradiated with an electron beam of suitable energy.

3.2.3.1 Principle

When a sample is irradiated by a beam of electrons of sufficient energy, the electrons in the ground state are excited to a higher energy state creating a hole. Subsequently, a higher energy electron falls to fill this hole and this difference in energy is emitted in the form of X-rays. An energy-dispersive spectrometer measures the energy and number of the emitted X-rays. These characteristic X-rays help identify the elemental composition of the sample and its distribution as well.¹⁷

3.2.3.2 Application

EDX was used in this study to investigate the elemental distribution in the synthesized powder samples. EDX experiment was carried out in tandem with SEM imaging using the JEOL 6340 and 7600F with EDX detectors attached.

3.2.4 Transmission Electron Microscopy (TEM)

TEM makes use of the low wavelength of electrons to yield high resolution imaging of materials in the nano regime.

3.2.4.1 Principle

As seen in Figure 3-7, electron beam generated by the electron gun is focused upon the specimen to be imaged via condenser and objective lenses. For this purpose, very thin sample specimens are used to allow more electrons to pass through. The transmitted electrons striking the fluorescent screen produces the image. The higher density regions in the specimen appear darker in the image. The amplitude and phase contrast of the electron waves passing through the specimen are utilized to produce the image.

Figure 3-7. Configuration of a transmission electron microscope.¹⁸

3.2.4.2 Application

In this work, JEOL 2100F was used for TEM imaging purposes. The accelerating voltage was 200 kV. Gatan DigitalMicrograph software was used for the image analyses.

3.2.5 Selected Area Electron Diffraction (SAED)

SAED is employed for the semi-quantitative phase analysis of nanocrystalline samples.

3.2.5.1 Principle

When a beam of electrons is focused upon a crystalline sample, the electrons undergo diffraction upon satisfying the Bragg's law. A typical SAED pattern for a polycrystalline sample is presented in Figure 3-8. For crystalline samples, the SAED pattern comprises of bright spots while amorphous and polycrystalline materials produce ring patterns. The different phases have characteristic SAED patterns and hence by indexing the diffraction rings/spots, the phases can be identified.

Figure 3-8. Selected Area Electron Diffraction pattern from polycrystalline ZnO thin films.¹⁹

3.2.5.2 Application

In this work, SAED was carried in tandem with TEM microscopy in the JEOL 2100F with an intermediate-lens aperture of 20 μm diameter. SAED analyses were used to fingerprint the various phases present in the samples synthesized in this study. Gatan Digital

Micrograph and ImageJ software were used to index and analyze the SAED patterns.

3.2.6 Raman Spectroscopy

Raman spectroscopy is widely used vibrational spectroscopy to investigate solid, liquid as well as gaseous samples.

3.2.6.1 Principle

When monochromatic light interacts with a sample, it can undergo various kinds of scattering as shown in Figure 3-9. Raman spectroscopy utilizes the inelastic scattering of monochromatic light. In the case of Stokes Raman scattering, the energy of the re-emitted photons is lower than the incident beam while for anti-Stokes scattering, the energy of the emitted beam is higher. The shift in the energy can be correlated to the vibrational energy levels in the molecules of the sample.

Figure 3-9. Raman spectroscopy based on inelastic scattering.²⁰

3.2.6.2 Application

Raman spectroscopy is useful to analyze carbon materials as the different hybridization states have characteristic vibrational energy. For instance, the sp^2 bonded carbon atoms in graphite sheets have higher bond energy than the sp^3 bonded carbon in diamond. In this work, Raman spectroscopy was used to characterize the $FeSn_2$ /carbon composites to

investigate the disorder induced by ball milling. Witec Alpha 300 SR (Ar laser, 488 nm) was used for the purpose.

3.2.7 X-ray Photoelectron Spectroscopy (XPS)

XPS is a widely used surface-sensitive characterization technique to probe the elemental composition, chemical and electronic states of elements present in a material. The technique can be applied to a broad range of materials including powders and films.

3.2.7.1 Principle

XPS is carried out by irradiating the sample with a beam of X-rays and quantifying the kinetic energy and count of electrons that are subsequently emitted. The governing equation is as follows²¹:

$$E_b = h\nu - E_k - W$$

Where,

$h\nu$ is the source radiation energy

E_k is the kinetic energy of the photoelectron measured by the spectrometer

E_b is the binding energy of the electron

W is the work function of the spectrometer

By measuring the quantities on the right-hand side of the equation, the E_b value can be calculated. The E_b vs. intensity of the emission yield a characteristic XPS spectrum and serves as a fingerprinting tool for elemental analysis.

3.2.7.2 Application

In this work, XPS was used to determine the changes in the oxidation states of specific elements upon sodiation/desodiation reactions. The XPS measurements were performed by Latech services using a PHI-5400 equipment with Al Ka beam source (250 W) and position-sensitive detector (PSD). The binding energy resolution is 0.8 eV, angle resolution

is 45° and the detection limit is 80 K CPS. Base pressure of the measurement chamber is 3.0×10^{-7} Pa. The Ar ion (voltage 12 kV, current 4.2 mA) sputtering speed is 0.28 nm/s over an area of $400 \times 400 \text{ um}^2$.

3.3 Device Fabrication and Characterization

3.3.1 Coin cell assembly

The conventional coin cell fabrication method was adopted in this study to investigate the electrochemical performance. The electrodes comprised of active material, Super P carbon and carboxymethyl cellulose (CMC) binder in the ratio 3:1:1 respectively. Initially, the three components were mixed thoroughly in a mortar and pestle before stirring overnight in a mixture of water and ethanol (4:2 v/v) to form the slurry. The well-mixed slurry was coated on a copper foil via doctor blading and the coating was dried in ambient air overnight. The dried coating was then roll-pressed and punched into circular discs of 14 mm diameter. CR2016 coin cells were used for assembly inside an argon filled glovebox (MBRAUN). Porous glass fiber (Whatman, UK) was used as the separator and flattened disc of sodium metal (Sigma Aldrich) was used as the counter electrode for half-cell assembly. One molar NaClO_4 in propylene carbonate (PC) and fluoroethylene carbonate (FEC, 5% vol.) was used as the electrolyte.

3.3.2 Cyclic Voltammetry (CV)

CV is a widely used electrochemical characterization technique and provides information about the redox processes occurring at the electrode and their reversibility among others.

3.3.2.1 Principle

In coin cell configuration, CV is performed by cycling the potential of a working electrode against a reference/counter electrode. The potential is linearly swept at a fixed scan rate between two vertex potentials in a cyclic fashion and the resulting current is measured. The

plot of the current and the applied potential gives the cyclic voltammogram. The CV peaks (Figure 3-10) indicate the redox reactions taking place and their reversibility and stability.

Figure 3-10. Cyclic voltammogram depicting a single electron redox process.²²

3.3.2.2 Application

In this work, CV experiments were carried out in Solartron 1470E. The redox peak positions were determined, and potential windows were set from the CV measurements as well as the reversibility of the electrochemical reactions was ascertained.

3.3.3 Galvanostatic Charge Discharge (GCD)

GCD tests are used to determine the calendar life of batteries. Typically, the coin cells are charged and discharged over hundreds of cycles and the capacity retention is analyzed.

3.3.3.1 Principle

In GCD tests, a constant current is applied to the coin cell which charges and discharges the cell to the set cutoff voltages. The GCD profiles of capacity vs. potential provides valuable information regarding the thermodynamics and the chemical potential of the system. Additionally, the occurrence of phase transformations is indicated by the slope of the profile. Typically, a first order phase transformation is indicated by a flat plateau

whereas a smooth slope indicates the formation of a solid solution of sodium in the host material.

3.3.3.2 Application

In this work, Neware Battery Testing System (BTS) was used for the GCD experiments. The GCD tests were used to investigate the sodiation/desodiation capacities and the Coulombic efficiencies of the anode materials. Moreover, GCD tests at high current rates (rate performance tests) were carried out to determine the charging/discharging capability of the materials at different currents.

3.3.4 Electrochemical Impedance Spectroscopy (EIS)

EIS technique is useful to evaluate detailed kinetic information as well as monitor state of charge, investigate reaction mechanisms and identify electrode corrosion processes.

3.3.4.1 Principle

During EIS experiments, an AC signal of small amplitude is applied to the cell over a range of frequencies. The response from the cell is analyzed and the impedance is calculated. Equivalent circuit modelling is widely used to interpret the EIS results which are plotted in the complex plane as Nyquist plot or as magnitude and phase versus frequency in Bode plot. A typical EIS spectra for a half cell lithium battery is shown in Figure 3-11. The low frequency region has a sloping line which is indicative of the lithium diffusion kinetics and is denoted as the Warburg element in the equivalent circuit. The semicircle in the middle to high frequency region relates to the charge transfer as well as the electrode-electrolyte interfacial capacitance. The semicircle diameter is indicative of the charge transfer resistance (R_{CT}) while the point of intersection of the semicircle in the high frequency region gives the solution resistance (R_s).

Figure 3-11. Impedance spectra and the corresponding equivalent circuit of a lithium-ion battery illustrated as Nyquist plot.²²

3.3.4.2 Application

In this work, EIS studies were carried out using a Solartron 1470E by applying an AC signal of amplitude 10 mV over a frequency range of 0.01 Hz to 100 kHz at room temperature. The charge transfer and mass transport details of the various anode materials synthesized in this work were investigated by EIS technique.

3.3.5 Operando X-ray Diffraction

Operando XRD or in situ XRD is useful to study the phase and structural transformation in the active materials upon the sodiation/desodiation reactions as and when the reactions are occurring.

3.3.5.1 Principle

The operando XRD measurements make use of a specially designed electrochemical cell (Figure 3-12) set-up in the XRD unit so that the electrochemical processes and the XRD measurements are carried out in parallel. The XRD measurements taken during the electrochemical charge-discharge processes in the cell would provide information

regarding the structural changes to the active material upon sodiation/desodiation reactions. Many reaction intermediates and unstable compounds formed in situ can be revealed using this technique.

Figure 3-12. Operando XRD electrochemical cell setup.²³

3.3.5.2 Application

In this work, a modified cell for the Rigaku SmartLab X-ray diffractometer (200 mA, 45 kV) in reflection mode, with copper ($1.54 \text{ \AA}$) as the X-ray source. The technique was used to characterize FeSbO_4 anode during sodiation/desodiation process.

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Chapter 4

Investigating the carbon matrix induced performance of Sn-rich FeSn₂ alloy anodes for sodium-ion battery

In this study, FeSn₂ alloy was synthesized by a facile solvothermal technique and the electrochemical performance of the alloy anode was evaluated. While the alloy delivered high capacities, the cycle life was limited. The cycle life was dramatically improved by fabricating FeSn₂/carbon composites via high-energy ball milling technique. The ball milling process enabled the encapsulation of the alloy particles in the carbon matrix. The embedding of the FeSn₂ particles in the carbon matrix was found to buffer the volume changes and thereby enhance the calendar life. Additionally, the influence of the type of carbon matrix was investigated for the commercially available graphite, graphene and Super-P carbons.

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4.1 Introduction

The need for high capacity anodes for sodium-ion batteries have been expounded in the recent literature.^{1,2} The conventional anode for LIBs, graphite has been found unsuitable for intercalating sodium-ions. Moreover, alloying and conversion-reactions based anodes possessing high gravimetric and volumetric capacities are essential to keep the sodium-ion batteries cost-effective for large format batteries.³ Among others, Sn possesses high theoretical capacity of 847 mAh g⁻¹ at adequately low potential and is cheap and abundant, making it suitable alloying anode for sodium-ion batteries. However, the poor cycling stability of Sn has remained an issue curbing its practical application.⁴⁻⁶

Previously, among the various intermetallic anodes of Sn investigated for LIBs, FeSn₂ exhibited enhanced electrochemical performance in terms of capacity and cycling stability.⁷ In this work, Sn-rich intermetallic FeSn₂ is explored as an anode material for sodium-ion battery. Nanostructured FeSn₂ was synthesized by facile and scalable solvothermal technique. Commercially available Graphite, Super P carbon and Graphene were used to fabricate FeSn₂/Carbon composites. High-energy ball milling technique was employed to fabricate the FeSn₂/carbon composites. The electrochemical performance of the materials was investigated in the coin cell assemblies and the effect of weight percent of graphite on the cycling stability of FeSn₂/Graphite composite was investigated. Moreover, the influence of the type of carbon matrix on the cycling performance was also investigated.

4.2 Experimental Methods

4.2.1 Material synthesis

The synthesis of FeSn₂ powder was carried out via solvothermal method. Initially, 2 mmol of tin (II) chloride (Alfa Aesar) and 1 mmol of iron ((II) chloride (Alfa Aesar) were mixed together in 25 ml ethanol. The solution was then transferred to a 45 ml Teflon-lined autoclave (Parr instruments) and stirred for one hour. Thereafter, sodium borohydride (Strem Chemicals) solution (5 ml, 5 M in ethanol) was added dropwise to the solution. The

autoclave was then sealed immediately and loaded to the oven for heating up to a temperature of 180 °C and held for 4 h to enable the reaction. Following the reaction, the autoclave was allowed to cool down to room temperature. The solution was removed from the autoclave and was centrifuged to obtain the FeSn₂ powder. The powder was washed thrice in ethanol to remove any impurities. Finally, the powder was dried in vacuum oven overnight before characterization and testing.

The synthesis of FeSn₂-carbon composites was carried out by high-energy ball-milling technique (SPEX 8000D, USA), making use of the commercially available Graphite (Sigma Aldrich), Super-P carbon (Timcal) and Graphene (Carborene). Prior to the experiment, the ball mill vials, balls and the powders were dried in vacuum oven overnight and transferred to the Ar-filled glovebox. The FeSn₂ powder and carbon were weighed keeping the ratio of FeSn₂ to carbon as 3:2 for all three composites and transferred to the ball mill vials. The ball-mill vials were sealed inside the glovebox before taken out and the ball-milling of the powders were carried out for four hours with a ten minutes stop time after every hour to allow equipment to cool down.

4.2.2 Material characterization

Bruker D8 Advance X-ray diffraction (XRD) using CuK α radiation (1.5405 Å) was used for the phase analysis of the FeSn₂ powder and TOPAS V4 software package was used for the Rietveld refinement analysis. Field emission scanning electron microscope (FE-SEM, JEOL JSM 6340F) enabled the morphological investigation of the powders. JEOL JSM 2100F was used to obtain the high-resolution transmission electron micrographs of the powders as well as the selected area electron diffraction patterns. Raman spectroscopy of the powders was carried out by using Witec Alpha 300 SR (Ar laser of 488 nm wavelength and 20 mW continuous power).

4.2.3 Electrochemical characterization

The investigation of electrochemical performance was carried out in conventional coin cell assemblies (CR2016). Initially, the electrodes were fabricated via slurry coating method. Typically, FeSn₂ powder, carbon and Polyvinylidene fluoride (PVdF) binder were mixed

in the ratio 6:2:2 with sufficient n-methyl pyrrolidone solvent to make a slurry. The slurry was then coated on copper foil via doctor blade and the coating was dried overnight in the oven. The electrodes for assembly were then cut out from the dried foil in the form of circular disks of diameter 16 mm. The electrodes were dried overnight in vacuum oven along with the coin cell parts, prior to the coin-cell assembly. The assembly of coin cells was carried out in Ar-filled glovebox (MBRAUN) with controlled atmosphere ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm). The counter electrode comprised of flattened Na metal disk (Sigma Aldrich) and the porous glass fiber (Whatman, UK) served as the separator. An in-house prepared 1M NaClO₄ in ethylene carbonate: propylene carbonate (1:1 v/v%) was used as the electrolyte. The crimped coin cells were then tested in NEWARE battery testing system for galvanostatic charge-discharge tests and rate performance tests. Additionally, Solartron 1470E was used for the cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurements.

4.3 Results and discussion

4.3.1 Morphology and phase characterization of FeSn₂ powder

The morphological characterization of the synthesized FeSn₂ powder was carried out with field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). Nanostructured micron-sized aggregates were observed in the FE-SEM micrographs of the FeSn₂ powder (Figure 4-1a). The high-resolution transmission electron micrograph (HR-TEM) of FeSn₂ powder (Figure 4-2b) shows the *d*-spacing in the (211) lattice confirming the tetragonal structure (PDF card no. 01-073-2030).⁸

The phase purity of the synthesized FeSn₂ powder was analyzed via powder XRD and Rietveld refinement techniques. The powder XRD pattern comprising of sharp peaks attest the crystallinity and phase purity of the powder. Additionally, the broad peaks indicate the presence of nanosized particles in the powder. The synthesized FeSn₂ powder was found to conform to the tetragonal structure. Rietveld refinement yielded the lattice parameters

calculated as $a = 6.525$ and $c = 5.331$ Å in the $I4/mcm$ space group which is in agreement with the published literature.⁸

Figure 4-1. (a) FESEM image and (b) HR-TEM image of FeSn₂ powder. (c) X-ray diffraction pattern of the synthesized FeSn₂ powder.

4.3.2 Electrochemical performance of the pristine FeSn₂ anode

Initially, the sodiation/desodiation reaction of the FeSn₂ alloy was investigated by cyclic voltammetry (CV) at a scan rate of 0.1 mV s^{-1} as depicted in Figure 4-2a. A broad peak at $\sim 0.5 \text{ V}$ vs. Na was observed during the initial scan from open circuit voltage to 5 mV.

Moreover, this peak was absent in the subsequent cycles and could be ascribed to the initial sodiation and electrolyte decomposition leading to the formation of solid electrolyte interphase.⁹ Upon complete sodiation reaction close to 5 mV, the formation of Na₁₅Sn₄ occurs according to the following reaction:^{8, 10}

During the desodiation cycle upto 2 V vs. Na, various oxidation peaks at ~ 0.09, 0.24, 0.71 and 0.85 V vs. Na were observed, which signify the desodiation reactions and the formation of the various Na_xSn_y phases.^{11, 12}

The electrochemical performance of the pristine FeSn₂ was investigated via galvanostatic charge-discharge tests as shown in Figures 4-2b. A voltage window of 0.005–2 V vs. Na was chosen and a specific current of 100 mA g⁻¹ was applied during the cycling test. The pristine FeSn₂ showed high capacity for the initial cycles. However, the capacity deteriorated within the first 20 cycles. Such a rapid deterioration in electrochemical performance could be attributed to the large volume changes occurring during the alloying/de-alloying reactions and the accompanying pulverization and loss of electronic contact. Hence, a buffer matrix such as carbon could possibly alleviate the volume changes associated with the sodiation/desodiation reactions and improve the cycling stability of the alloying anode. In this regard, FeSn₂-carbon composites were synthesized via high-energy ball milling and their electrochemical performance was evaluated.

Figure 4-2. (a) Cyclic voltammogram of FeSn₂ vs. Na. (b) Galvanostatic cycling performance of FeSn₂ anode.

4.3.3 Preparation of FeSn₂/Carbon composites

Initially, FeSn₂-Graphite composites were fabricated via high-energy ball milling for various weight ratios of FeSn₂: Graphite. Although the ball-mill vials were sealed in inert atmosphere, to further ensure that the FeSn₂ powder retained the phase purity during the ball-milling process, the XRD profiles of the composites were analyzed (Figure 4-3a). The absence of any impurity peaks suggest that no oxidation or side reactions occurred during

the ball-milling process. Furthermore, Raman spectroscopy was utilized to investigate the disorder induced in the composites during the high-energy ball milling process. It was observed that the FeSn₂-G (3:2) composite had a high I_D/I_G ratio which could be due to the strain induced as well as the embedding of the FeSn₂ nanoparticles in the graphitic matrix.^{13, 14} The I_D/I_G ratio was found to decrease to 0.8 for the FeSn₂-G (1:1) composite which had higher weight percentage of graphite, possibly suggesting the poor embedding of the FeSn₂ powder in the graphite matrix. Following the fabrication of the FeSn₂-Graphite composites, the electrochemical performance was evaluated.

Figure 4-3. (a) XRD pattern and (b) Raman Spectra of the ball milled FeSn₂/Graphite composites.

4.3.4 Electrochemical performance of FeSn₂/Graphite composites

To gauge the cycling stability, pristine FeSn₂ and FeSn₂-Graphite composites were evaluated in the coin cell assemblies in the potential range 0.005-2 V vs. Na at a specific current of 100 mA g⁻¹. As seen in Figure 4-4a, the addition of graphite to FeSn₂ visibly improves the cycling stability. Moreover, the ratio of FeSn₂ to Graphite has been optimized to deliver enhanced cycling stability as observed for the FeSn₂-G (3:2) which is stable for more than 200 cycles. It was found that both low and high graphite content (FeSn₂-G (9:1) and FeSn₂-G (1:1) composites respectively) failed to improve the cycling stability, possibly due to the poor encapsulation of FeSn₂ in the former and the pronounced influence of the graphite with low sodiation capacity in the latter. Among others, the FeSn₂-G (3 :2)

composite demonstrated excellent electrochemical performance with a capacity retention of ~70% at the end of 200 cycles (Figure 4-4b) evidently due to the ideal encapsulation of FeSn₂ particles in the graphite matrix.

As depicted in Figure 4-4c, the FeSn₂-Graphite composite electrodes were cycled at different current rates ranging from 0.05-1 A g⁻¹ in order to investigate the suitability of the composite anodes for different applications requiring both high and low current inputs. The FeSn₂-G (3 :2) composite outperformed others, further demonstrating the enhanced electrochemical performance delivering ~200 mAh g⁻¹ at a high current of 1 Ag⁻¹. The preliminary results are promising, considering the requirements of the high-power applications including hybrid electric vehicles calling for high power capabilities. Additionally, the electrochemical behavior of both pristine FeSn₂ and the FeSn₂-Graphite composites were investigated via electrochemical impedance spectroscopy (EIS). A frequency range of 0.1 MHz to 10 mHz was chosen and an AC perturbation voltage of amplitude 10 mV was applied. The Nyquist plots (Figures 4-4d) demonstrate the charge transfer process at high frequency region, indicated by the depressed semi-circle and mass transfer process at low frequency region-indicated by the sloping line.¹⁵ Among others, the FeSn₂-Graphite (3: 2) composite demonstrated the lowest charge transfer resistance and therefore corroborates the outstanding electrochemical performance.¹⁶ The larger charge-transfer resistance of the FeSn₂-G (1 :1) indicated by the larger diameter, is possibly due to the electrode inhomogeneities caused by the high graphite content and the accompanied loss of electronic contact between the FeSn₂ particles and the graphite/binder, leading to uneven local stress-strain distribution.¹⁷ The results further suggests the inevitability to optimize carbon content to achieve enhanced electrochemical performance .

Figure 4-4. (a) Galvanostatic cycling performance of the FeSn₂/Graphite composites. (b) Enhanced cycling stability of the FeSn₂-G (3:2) composite. (c) Rate performance and (d) EIS spectra of the FeSn₂/Graphite composites.

4.3.5 Effect of carbon matrix on the cycling performance

The morphology of the commercial carbon powders used for fabricating the FeSn₂/carbon composites are shown in Figure 4-5a-c. Figure 4-5d shows the powder XRD pattern of the FeSn₂/Carbon composites obtained after the high energy ball milling process. The crystallinity of FeSn₂ was preserved, and no phase changes or oxidation occurred during the ball milling process.

Figure 4-5. FESEM images of the (a) Graphite flakes, (b) Super P carbon, (c) Graphene sheets, used for making composites. (d) XRD pattern of the ball milled FeSn₂/carbon composites.

The potential profiles as well as the galvanostatic cycling performance of the FeSn₂ anode as well as the FeSn₂/Carbon composites are presented in Figure 4-6. The FeSn₂/Carbon composites showed enhanced cycling performance when compared to the pristine as well as ball-milled FeSn₂. This further confirms the utility of the carbon matrix to sustain enhanced cycle life when compared to the pristine and ball-milled FeSn₂ which could not endure the volume changes and resulted in rapid capacity fading within the first 20 cycles. By ball-milling FeSn₂ along with carbon, the FeSn₂ particles are encapsulated in the carbon matrix and the composite demonstrates excellent electrochemical performance due to the effective buffering of the stresses during the sodiation/desodiation reactions.¹⁸ Furthermore, the following reasons also contribute to the enhanced cycling electrochemical performance of the FeSn₂/Carbon composites: (a) The encapsulation of FeSn₂ particles in the carbon matrix aids in the formation of a stable solid electrolyte interphase (SEI) that minimizes

the exposure of the freshly formed alloy surface (during pulverization) to electrolyte.¹⁹ (b) The high conductivity of the carbon matrix would benefit the rate performance and additionally, the matrix would help to suppress the agglomeration of the alloy particles as well.²⁰

Figure 4-6. Potential profiles of (a) FeSn₂ (b) Ball milled FeSn₂ (c) FeSn₂-Graphite (d) FeSn₂-Super P (e) FeSn₂-Graphene composites. (f) Galvanostatic cycling performance of the FeSn₂/carbon composites.

Furthermore, the rate performance of the FeSn₂-Carbon composites was elucidated by cycling at different specific currents (0.02-1 A g⁻¹) in the potential window 0.5 mV -2 V vs. Na (Figure 4-7). It was found that the composites could tolerate the various applied current rates and delivered ~200 mAh g⁻¹ at a high current of 1 A g⁻¹. Once the high current pulse was lowered to 20 mA g⁻¹, the composite recovered the capacity, further attesting the fast Na-ion storage performance of the composites. Additionally, the electrochemical impedance spectroscopy (EIS) of the pristine FeSn₂ and FeSn₂-carbon composites was investigated and is presented in the Nyquist plots (Figure 4-7). A frequency range of 0.1 MHz to 10 mHz was chosen and an AC perturbation voltage of amplitude 10 mV was applied. The Nyquist plots demonstrate the charge transfer process at high frequency region, indicated by the depressed semi-circle and mass transfer process at low frequency region- indicated by the sloping line.^{15, 21} Among others, the smaller charge transfer resistance of the FeSn₂-Graphite composites further corroborate the outstanding electrochemical performance.¹⁶ The results elucidate the enhanced electrochemical performance achieved by the alleviation of the accompanying stresses and strains in sodiation/desodiation reactions via encapsulating the alloy particle in a carbon matrix.

Figure 4-7. (a)Rate performance and (b) EIS spectra of FeSn₂/carbon composites.

To visualize the distribution of the FeSn₂ alloy particles in carbon composites, HR-TEM was carried out and the images (Figure 4-8) clearly show the encapsulation of the FeSn₂ particles within the carbon matrix. Additionally, the SAED patterns (Figure 4-8 inset)

comprising of a diffuse set of rings corresponding to the amorphous carbon matrix, along with the bright spots indicating the crystalline FeSn₂ alloy phase, further provide unambiguous evidence for the FeSn₂-carbon composite structure. It is possibly this encapsulation that enables the formation of a stable SEI layer on the anode surface and enables long-term cycling performance by minimizing the capacity drop.

Figure 4-8. TEM images of (a, b) FeSn₂/Graphite, (c, d) FeSn₂/Super P carbon, (e, f) FeSn₂/Graphene composites.

4.4 Conclusions

In conclusion, Sn-rich alloy FeSn₂ nanoparticles were synthesized via facile solvothermal technique and the electrochemical performance was evaluated for sodium-ion battery anode configuration. The cycling stability was significantly enhanced by fabricating FeSn₂/carbon composite anodes as a result of the effective buffering of the stresses induced during sodiation/desodiation reactions. The commercially available carbon materials such as graphite, Super-P carbon and graphene were utilized for making the composites. The effective encapsulation of the FeSn₂ particles in the carbon matrix resulted in enhanced cycle life. Hence, a scalable and transferable high energy ball milling technique was demonstrated for the synthesis of alloy/carbon composite anodes and the influence of the carbon matrix was investigated to enhance the cycle life for sodium-ion batteries.

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Chapter 5

Synthesis of Sb-rich Fe-Sb alloy ribbons via melt-spinning process: investigation and performance evaluation as anodes for sodium-ion battery

In this chapter, a high-throughput, scalable and industrially viable melt-spinning/rapid solidification technique is utilized to synthesize Fe-Sb alloy ribbons. The phase and morphological features of the alloy ribbons were characterized which revealed nanocrystalline and amorphous features of the alloy ribbons. The electrochemical performance of the alloy ribbons was investigated and the sodiation/desodiation mechanism was explored. Furthermore, preliminary investigations were carried out in a full-cell sodium-ion battery configuration by coupling with a sodium manganese oxide cathode. The full-cell demonstrated high capacity and Coulombic efficiency, attesting the suitability of the alloy anode for practical applications.

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5.1 Introduction

Antimony-based anode materials have been widely explored for SIBs due to the high sodiation capacities, adequate sodiation/desodiation potentials and low cost of these materials.^{1, 2} Bare Sb can alloy with Na to form Na₃Sb upon complete sodiation, resulting in a capacity of 660 mAh g⁻¹.³ Despite the high capacity, the poor calendar life of Sb anode is a serious issue preventing its practical utilization and commercialization. Various strategies have been employed to mitigate the issue of poor cycling stability including the use of carbon matrix, controlling the particle morphology and size, among others.⁴⁻¹¹ However, most of these approaches require complex synthesis protocols, provide low yield and suffer from poor scalability issues. In this context, the synthesis of Sb-rich intermetallic anode materials via high-throughput and industrially viable technique such as melt-spinning is of great interest.

Melt-spinning is commercially used for the fabrication of thin alloy sheets with several inches in width. The high quenching rates of the order of $\sim 10^6$ K s⁻¹ can impart the alloy with intriguing microstructure with both crystalline and amorphous landscapes.^{12, 13} This work aims at the synthesis of Sb-rich Fe-Sb alloy ribbons via melt-spinning process and the investigation of the electrochemical performance of the intermetallic as anode for sodium-ion battery. The topography and the microstructure of the alloy ribbons have been investigated. The sodium-storage mechanism in the alloy anode is also investigated and the practical use of the alloy anode is preliminarily investigated in a sodium-ion battery full-cell configuration as well.

5.2 Experimental methods

5.2.1 Material synthesis

Antimony powder (99.5%, Alfa-Aesar) and Iron powder (99+%, Alfa-Aesar) were weighed in the molar ratio and cold pressed into pellets. A single-roller melt-spinner (Edmund Bühler GmbH, Melt Spinner SC) with a 20 cm diameter Cu wheel was utilized to prepare

the Fe-Sb alloy ribbons from the pressed pellets inside an Ar-filled chamber. The distance between the bottom of the nozzle and the surface of the copper wheel was set at 50 mm, and the rolling rate of the wheel was 50 Hz. The pellet was melted via induction heating to molten liquid and then ejected through the slotted nozzle by means of pressurized Ar gas. The molten liquid rapidly solidified into very thin flakes upon contact with the water-cooled copper wheel.

The cathode material, sodium manganese oxide (NMO) was synthesized by a solution-based technique.¹⁴ Briefly, NH_4HCO_3 was dissolved in deionized water, followed by a dropwise addition of ethanol (10% v/v of the NH_4HCO_3 solution). Following this, a solution of MnSO_4 in deionized water was added and additionally, CoSO_4 was added to the MnSO_4 solution to achieve a 10% ratio. The solution was stirred at room temperature. The precipitates were filtered and washed followed by annealing in air at 400 °C for 5 h to form MnO_2 . Afterwards, the product was dispersed in a solution of NaOH in deionized water and ethanol. Following this, both ethanol and water were evaporated, and the residue was first annealed at 320 °C in air for 3 h, followed by an annealing step in air at 800 °C for 4 h and further annealing at 610 °C for 9 h and lastly quenched to room temperature.

The electrode preparation for the cathode material is similar to that of the anode, except that aluminium foil was used for the cathode slurry coating. Prior to full-cell assembly, the MS_FeSb anode was pre-treated in half-cell assembly in Swagelok fittings for two galvanostatic cycles to overcome the irreversible capacity loss in the first cycle as well as to ensure reversible capacity observed from the half-cell assembly. The cycled anode was then used for the full-cell assembly which was carried out in coin cell configuration with NMO:MS_FeSb active material ratio 3:1 to balance the capacity.

5.2.2 Material Characterization

Phase structure of the alloy ribbons was 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°–80°. Field emission scanning electron microscope (FESEM) (JEOL, JSM-7600F) and high-

resolution transmission electron microscope (HR-TEM) (JEOL, JEM-2100F) with energy dispersive X-ray spectroscopy (EDX) attachment are used for topological and elemental composition analysis of the melt spun flakes. For HR-TEM, the sample is first ground in mortar and pestle and dispersed in ethanol and then dripped onto copper grid and dried at room temperature.

5.2.3 Electrochemical Characterization

The electrochemical evaluation of the materials was carried out in coin cell (CR2016) assemblies. The anodes were fabricated by mixing the Fe-Sb alloy ribbons, super-P carbon (Timcal) and carboxymethyl cellulose (Sigma-Aldrich) in the weight ratio of 3:1:1 and dispersed in de-ionized water and stirred overnight. The slurry was then cast onto a copper foil (Hohsen, Japan) and dried in air at ~ 60 °C for 12 h. Circular electrodes of diameter 14 mm and active material loading of ~ 1.5 -2 mg cm⁻² were punched out and dried further in vacuum oven at 100 °C for 12 h prior to coin cell assembly. The coin cells were then assembled in an argon-filled glovebox (MBRAUN) with moisture and oxygen content less than 1 ppm. Flattened sodium metal disk (Sigma-Aldrich) was used as the counter electrode, porous glass fiber (Whatman Cat. No. 1825-047, UK) as the separator and a solution of 1 M NaClO₄ (Sigma-Aldrich) in propylene carbonate (PC, Sigma-Aldrich) and 5 vol. % fluoroethylene carbonate (FEC) as the electrolyte. Cyclic voltammetry was performed with an electrochemical workstation (Solartron 1470E) in the potential range of 0.005–2.5 V (*vs.* Na). The cells were cycled galvanostatically between 0.005 and 2.5 V (*vs.* Na) at various current densities using the NEWARE multi-channel battery test system.

5.3 Results and discussion

The schematic of the melt-spinner used for the synthesis of Fe-Sb flakes is shown in Figure 5-1a. Initially, the Fe and Sb powders (1:2 molar ratio) are mixed homogenously in a mortar and pestle and cold pressed to a pellet. The pellet is then transferred to a quartz tube with slit nozzle and placed appropriately inside the RF induction heating coils. To prevent any oxidation, the quartz tube as well as the chambers are purged with Argon gas. When the

quartz tube is heated to high temperatures, the Fe and Sb powders melt, and the melt is then forced out of the nozzle by means of pressurized Argon gas. Upon contact with the water-cooled rotating copper wheel, the melt solidifies to form ribbons (Figure 5-1b) of nearly 20-40 mm length. Additionally, over 90% yield was achieved in the melt-spinning process which signifies the commercial implications of the synthesis technique.

Figure 5-1: (a) Graphical Illustration of the Preparation of Melt-Spun Fe-Sb Alloy Ribbons, (b) Digital Images, and (c) Microscopic Images Showing Appearance of Freshly Prepared Alloy Ribbons.

5.3.1 Phase and morphological characterization of alloy ribbons

The phase characterization of the synthesized Fe-Sb alloy ribbons (MS_Fe-Sb) was carried out by XRD analysis. The alloy ribbons produced high-intensity diffraction peaks suggesting their crystallinity (Figure 5-2a). The Rietveld refinement of the diffraction pattern confirmed the composition of the alloy (Figure 5-2c) to consist of FeSb₂ (88.38 %) and FeSb (11.62 %). The surface features of the alloy ribbons were examined by FESEM and HR-TEM techniques. The HR-TEM images of the alloy ribbons are presented in Figure 5-2d, e and they reveal the formation of nanocrystalline domains in an amorphous matrix. One such domain with a *d*-spacing of 0.285 nm is indexed in Figure 5-2e. Such a unique microstructure is produced due to the rapid cooling rates in the melt-spinning process that can arrest nucleation and grain growth. This further attests the significance of melt-

spinning technique to fabricate nanocrystalline alloy ribbons with high yield and scalability. The SEM-EDX measurements indicate the uniform distribution of Sb and Fe in the alloy ribbons (Figure 5-2 f-h).

Figure 5-2: (a) XRD pattern of the as-obtained Fe-Sb alloy ribbons (PDF numbers 01-075-1498 34-1184 (FeSb_2) and 34-1053 (FeSb)). (b) Crystal structures of FeSb_2 and FeSb alloys. (c) Phase

composition of the melt-spun alloy. (d, e) HR-TEM images of Fe-Sb alloy flakes. (f-h) SEM-EDX micrographs showing mapping of the flakes (blue label represents Sb; red label represents Fe).

5.3.2 Electrochemical performance and sodiation mechanism evaluation in half-cell sodium-ion battery assembly

The electrochemical performance of the alloy ribbons was then investigated in conventional coin cell assemblies. The Fe-Sb alloy ribbons were mixed thoroughly with Super P carbon and aqueous carboxymethyl cellulose binder solution in the ratio 3:1:1 and slurry coated onto a copper foil. The dried copper foil was then cut into circular disc electrodes to be assembled into the coin cells. 1 M NaClO₄ in propylene carbonate (PC) with 5 vol.% fluoroethylene carbonate (FEC) was used as the electrolyte. The coin cell was then charged and discharged for several cycles at a constant current of 50 mA g⁻¹. As seen in Figure 5-3a, the initial sodiation capacity was ~555 mAh g⁻¹ and the Coulombic efficiency was 81.3%. In the subsequent cycles, the Coulombic efficiency increased to 97-99%. After 80 cycles, ~95 % of the capacity was retained by the alloy anode. This enhanced cycling performance can be attributed to the unique nanocrystalline microstructure formed in the alloy via rapid solidification process which helps to alleviate the stresses induced during the sodiation/desodiation reactions. This is further validated by comparing the performance of physically mixed Fe-Sb and pristine Sb to that of melt-spun Fe-Sb alloy ribbons (Figure 5-3b). Furthermore, the MS_Fe-Sb alloy anode also exhibited excellent rate performance as evident from Figure 5-3c, d. The anode delivered ~300 mAh g⁻¹ at a high current rate of 1 A g⁻¹, further attesting the efficient conductive diffusion pathways realized in the melt-spun alloy anode.

Figure 5-3: (a, b) Galvanostatic cycling at 50 mA g⁻¹. (c) Rate performance and (d) Potential

profiles of MS_Fe-Sb at different specific currents from 50 to 1000 mA g⁻¹ in the potential window 0.005–2.5 V vs Na⁺/Na.

The sodiation mechanism of the MS_Fe-Sb alloy anode was investigated by cyclic voltammetry and ex situ XRD analysis. From the CV profile of the first cycle, a broad reduction peak close to 0.2 V vs. Na indicates the reduction of the electrolyte leading to the formation of the solid electrolyte interphase as well as the sodiation of the active material.^{15, 16} In the desodiation process, a sharp peak at ~0.86 V vs. Na indicates the de-alloying process. In the subsequent cycles, followed by the restructuration of the active material, the sodiation/desodiation peaks were seen to overlap indicating excellent reversibility and cycling stability.¹⁷ The ex situ XRD patterns of the sodiated/desodiated electrodes after the first and second cycles are presented in Figure 5-4b. Upon sodiation, the Fe-Sb alloy transformed to poorly crystallized Na₃Sb as seen from the weak diffraction peaks at ~19.1, 21.3 and 38.7 degrees (JCPDS #741,162).¹⁷ From the CV and the XRD profiles, the reaction mechanism can be deduced as follows:¹⁷

During the desodiation process, inactive amorphous Fe serves as both the conductive matrix as well as the buffer medium to alleviate the stresses associated with the reactions and the following reversible reactions take place:

Figure 5-4: (a) Cyclic voltammogram of MS_FeSb at 0.1 mV s^{-1} in the potential window 0.005–2.5 V vs Na^+/Na . (b) Ex situ XRD patterns of sodiated/desodiated electrodes.

Furthermore, the sodiation/desodiation kinetics of the MS_Fe-Sb alloy was investigated by the CV response at increased scan rates from 0.1-2 mV s⁻¹. As seen from Figure 5-5a, peak current increased as the scan rate was increased. The power law was utilized to plot the variation in the peak currents:

$$\log i_p = b \log v + \log a$$

where, i_p : peak current, v : scan rate, a and b : constants.

As evident from Figure 5-5b, for the peak currents, a linear relationship was observed between $\log(i)$ and $\log(v)$. The constant “ b ” value was calculated from the slope of the lines and for peaks 1, 2 and 3, “ b ” value corresponds to 0.72, 0.73 and 0.56 respectively. As the b values close to unity reveals pseudocapacitive behavior, for the alloy anode with b value in the range 0.5-0.7 suggests contributions from both solid-state diffusion and pseudo-capacitance which is a synergistic pair that explains the enhanced rate performance of the alloy anode as well.¹⁸ Additionally, the electrochemical impedance spectra attests the formation of a stable SEI as there is negligible increase in the diameter of the semicircle indicating charge transfer resistance of the anode after cycling as seen from the Nyquist plot (Figure 5-5c). Moreover, the sloping tail corresponds to the Warburg impedance at low-frequency region and implies the diffusion of Na⁺ ions into the anode.¹⁹

Figure 5-5: (a) Cyclic voltammogram of MS_Fe-Sb anode at different scan rates. (b) $\log(i)$ vs $\log(v)$ relationship of peaks 1–3. (c) EIS spectra of MS_FeSb fresh electrode and after 80 cycles.

5.3.3 Preliminary investigation of the Fe-Sb anode in full-cell sodium-ion battery configuration

To realize practical implementation of SIBs, it is vital to examine the electrochemical performance of the anode in full-cell configuration. In this regard, sodium manganese oxide (NMO) was synthesized following a previous reported protocol and was used as the cathode material.¹⁴ The morphology of the NMO powder was investigated using FESEM as depicted in Figure 5-5a. Uniformly distributed particles of nearly 5 μm diameter spheres was observed.

Figure 5-6: (a) FESEM image of the synthesized NMO powder. (b) Galvanostatic cycling performance of NMO cathode in half-cell assembly at 50 mA g⁻¹.

The synthesized NMO delivered a capacity of ~160 mAh g⁻¹ with an average sodiation potential of ~2.4 V vs. Na (Figure 5-6b, 5-7a). The MS_Fe-Sb anode was pretreated in half-cell configuration for two cycles prior to full-cell assembly. This is to mitigate the low Coulombic efficiencies in the initial cycles which would hamper the performance in full-cell configuration where Na⁺ ions are limited by the cathode.²⁰ The NMO/MS_Fe-Sb full-cell delivered a capacity of ~350 mAh g⁻¹ in the first cycle and retained close to 79% after 25 cycles (Figure 5-7b). The Coulombic efficiency was over 99% which signifies the high reversibility of the sodiation/desodiation processes in the NMO cathode and the MS_Fe-Sb anode couple. Upon full charge, the full-cell could power a white LED lamp as well (Figure 5-7c). Further optimizations can significantly improve the cycling life as well as the capacity of the full-cell.

Figure 5-7: Full cell performance of MS_FeSb alloy ribbons coupled with NMO cathode. (a) Potential profile and (b) cycling stability at specific current of 50 mA g⁻¹. (c) Photograph showing LED powered by NMO/MS_Fe-Sb couple.

5.4 Conclusions

In conclusion, a scalable and industrially viable melt-spinning technique was employed to synthesize Sb rich Fe-Sb alloy anode for sodium-ion batteries. The characteristic microstructure of the melt-spun alloy was found to enhance the cycling stability of the anode by mitigating the stresses induced upon the sodiation/desodiation reactions. The anode delivered high capacity of $\sim 466 \text{ mAh g}^{-1}$ with 95% capacity retention after 80 in half-cell sodium-ion battery. The preliminary full-cell study of NMO/MS_Fe-Sb couple attests the suitability of the anode for practical applications as a high capacity of $\sim 300 \text{ mAh g}^{-1}$ with high Coulombic efficiency ($>99\%$) was achieved. Further optimizations could improve the energy density as well as the cycling stability of the full-cell to make it suitable for practical applications.

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Chapter 6

Melt-spun ternary Fe-Sn-Sb alloys: tuning the microstructure to enhance the cycling stability for sodium-ion battery

In this study, ternary Fe-Sn-Sb alloys were synthesized via melt-spinning technique. The phase and characteristic microstructural features of the alloy ribbons were explored. The electrochemical performance of the alloys was investigated and the sodiation/desodiation mechanism was examined. The nanocrystalline domains in the alloys were found to mitigate the stresses induced during the sodiation/desodiation reactions. Moreover, the ternary anode was coupled with an NaVPO_4F cathode which delivered high voltage and energy density. The preliminary electrochemical results exhort the capability to utilize the ternary anode for high-energy density sodium-ion batteries.

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6.1 Introduction

SnSb crystallizes in the rock salt structure with alternating Sn and Sb blocks.¹ As both Sn and Sb are active for sodium storage, SnSb alloy can deliver high sodium storage capacity. However, recent investigations have revealed the huge volume changes and the rapid capacity fading occurring in the SnSb anode.^{2, 3} Various strategies have been tested to improve the cycling stability of the SnSb anode for sodium-ion batteries. Various groups have synthesized SnSb nanocrystals, SnSb/carbon composites as well as porous SnSb particles to improve the cycling stability.⁴⁻⁷ However, most of these synthesis protocols make use of toxic reagents as well as produce low yields, making them unfit for practical applications.

In this work, the ternary Fe-Sn-Sb system (Figure 6-1) is explored and the cycling stability of SnSb is dramatically improved by tuning the microstructure of the ternary Fe-Sn-Sb alloy. Scalable and industrially viable melt-spinning/rapid-solidification process was employed to synthesize the ternary alloy ribbons. The electrochemical performance of the alloy ribbons was explored, initially in half-cell configuration and then the optimized ternary alloy anode was coupled with a NaVPO₄F cathode to study the full-cell sodium-ion battery performance.

Figure 6-1: Fe-Sb-Sn isothermal section of ternary phase diagram. ©Springer & Material Phases Data System (MPDS), Switzerland & National Institute for Materials Science (NIMS), Japan, 2016.⁸

6.2 Experimental methods

6.2.1 Material synthesis

Iron powder (99+%, Alfa-Aesar), Antimony powder (99.5%, Alfa-Aesar) and Tin powder (99+%, Alfa-Aesar) were weighed in the molar ratio and cold pressed into pellets. A single-roller melt-spinner (Edmund Bühler GmbH, Melt Spinner SC) with a 20 cm diameter Cu wheel was utilized to prepare the Fe-Sn-Sb alloy ribbons from the pressed pellets inside an Ar-filled chamber. The distance between the bottom of the nozzle and the surface of the copper wheel was set at 50 mm, and the rolling rate of the wheel was 50 Hz. The pellet was melted via induction heating to molten liquid and then ejected through the slotted nozzle by means of pressurized Ar gas. The molten liquid rapidly solidified into very thin flakes upon contact with the water-cooled copper wheel.

The cathode material, sodium vanadium fluorophosphate (NVPF) was synthesized as per a previous report. Briefly, cetyltrimethylammonium bromide (CTAB, 1 mmol) was dissolved in a mixture of ethanol and deionized water (12:1). The solution was sonicated for 90 minutes. NaF (4 mmol), oxalic acid (4 mmol) and V_2O_5 (2 mmol) were added to the solution and stirred for 30 minutes. Afterwards, $NH_4H_2PO_4$ (4 mmol) was added to the solution and then stirred for 24 hours. Next, the solvent was evaporated, and the residue was ground in a mortar and pestle, followed by an annealing step in Ar at 800 °C for 5 h to obtain the $NaVPO_4F$ phase.

The electrode preparation for the cathode material is as described in section 2.3, except that aluminium foil was used for the cathode slurry coating. Prior to full-cell assembly, the FeSnSb anode was cycled in a half-cell assembly for two galvanostatic cycles to overcome the irreversible capacity loss in the first cycle as well as to ensure reversible capacity observed from the half-cell assembly. The cycled anode was then used for the full-cell assembly which was carried out in coin cell configuration with NVPF:FeSnSb active material ratio 5:1 to balance the capacity.

6.2.2 Material Characterization

Phase structure of the alloy ribbons was 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°–80°. X-ray photoelectron spectroscopy (XPS) was carried out using Kratos AXIS Supra XPS equipped with an automated dual anode (Al/Ag K_α) X-ray monochromatic source. Field emission scanning electron microscope (FESEM) (JEOL, JSM-7600F) with energy dispersive X-ray spectroscopy (EDX) attachment and high-resolution transmission electron microscope (HR-TEM) (JEOL, JEM-2100F) were used for topological and elemental composition analysis of the melt spun flakes. For HR-TEM, the sample was first ground in mortar and pestle and dispersed in ethanol and then dripped onto copper grid and dried in vacuum oven at 60 °C.

6.2.3 Electrochemical Characterization

The electrochemical evaluation of the materials was carried out in coin cell (CR2016) assemblies. The anodes were fabricated by mixing the Fe-Sn-Sb alloy ribbons, super-P carbon (Timcal) and carboxymethyl cellulose (Sigma-Aldrich) in the weight ratio of 8:1:1 and dispersed in de-ionized water and stirred overnight. The slurry was then cast onto a copper foil (Hohsen, Japan) and dried in air at ~ 60 °C for 12 h. Circular electrodes of diameter 14 mm and active material loading of ~ 1.5 -2 mg cm⁻² were punched out and dried further in vacuum oven at 100 °C for 12 h prior to coin cell assembly. The coin cells were then assembled in an argon-filled glovebox (MBRAUN) with moisture and oxygen content less than 1 ppm. Flattened sodium metal disk (Sigma-Aldrich) was used as the counter electrode, porous glass microfiber (Whatman Cat. No. 1825-047, UK) as the separator and a solution of 1 M NaClO₄ (Sigma-Aldrich) in propylene carbonate (PC, Sigma-Aldrich) and 5 vol. % fluoroethylene carbonate (FEC) as the electrolyte. Cyclic voltammetry was performed with an electrochemical workstation (Solartron 1470E) in the potential range of 0.005–2 V (*vs.* Na). The cells were cycled galvanostatically between 0.005 and 2 V (*vs.* Na) at various current densities using the NEWARE multi-channel battery test system.

6.3 Results and discussion

6.3.1 Alloy ribbons: synthesis and characterization

Commercially available micron-sized metal powders (Figure 6-2) of Fe, Sn and Sb were used as the precursors for the melt-spinning process. Pure SnSb alloy ribbons were synthesized by the melt-spinning technique with Sn and Sb in 1:1 molar ratio. Additionally, Fe-Sn-Sb ternary alloy ribbons were synthesized in the similar route with different concentrations of Fe.

Figure 6-2. FESEM images of the metal powders of (a) Fe (b) Sn (c) Sb, used for the melt-spinning process.

According to the ternary phase diagram, $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ is the ternary single phase that exists while for other concentrations of Fe, there exists multi-phase fields. The atomic percentage of Fe in the Fe-Sn-Sb alloys were varied from 0.25-1.45 to synthesize $\text{Fe}_{0.25}\text{SnSb}$, $\text{Fe}_{0.5}\text{SnSb}$, FeSnSb and $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ alloys. The optical microscopy images of pure SnSb and FeSnSb alloy ribbons which are millimeters in width are presented in Figure 6-3.

Figure 6-3. Optical microscopy images of the melt-spun ribbons of (a) SnSb and (b) FeSnSb.

As evident from Figure 6-4a, the SnSb alloy as well as the Fe-Sn-Sb alloys are found to be crystalline in nature. The SnSb ribbons matched well with the trigonal crystal system in the $R\text{-}3mR$ space group (ICSD #197512).¹ The addition of Fe at various concentrations ranging from 0.25-1.45 was found to result in a two-phase alloy composition consisting of SnSb and $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ phases.⁹ The FESEM and HR-TEM investigation (Figure 6-4: b-e) of the alloy ribbons indicated the formation of nanocrystalline domains in an amorphous milieu. For instance, the FeSnSb alloy had nanocrystalline domains of both SnSb and

$\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ phases in various orientations (Figure 6-4e). One of the domains had d-spacing of 3.0534 Å corresponding to (202) plane in SnSb while the domain with d-spacing of 2.9691 Å corresponds to (101) plane in $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$. Furthermore, the EDX analysis showed uniform atomic distribution of Sn/Sb/Fe throughout the alloy ribbons.

Figure 6-4: (a) XRD patterns of the Fe-Sn-Sb alloy ribbons. (b) FESEM-EDX spectra and (c) HR-TEM image of SnSb alloy ribbon. (d) FESEM-EDX spectra and (e) HR-TEM image of FeSnSb alloy ribbon.

6.3.2 Electrochemical performance and sodiation mechanism

The cyclic voltammetry and galvanostatic charge-discharge tests of pure SnSb anode are presented in Figure 6-5. The SnSb anode delivered high capacity close to 600 mAh g⁻¹ in the initial cycles but could sustain such high capacities for only less than 15 cycles.

Figure 6-5. (a) CV of SnSb anode at 0.1 mV s⁻¹ (second cycle) and (b) Cycling at 50 mA g⁻¹ in the potential window 5 mV-2 V vs. Na.

The cyclic voltammogram peaks of SnSb anode reveals the following sodiation/desodiation reactions:⁴

Sodiation:

Desodiation:

The inclusion of Fe to form the ternary phases was found to improve the cycling stability (Figure 6-6). The ternary single phase Fe_{1.45}Sn_{0.5}Sb_{0.5} for instance, exhibited good cycling

stability but low capacity due to the higher dead weight of electrochemically inactive Fe. The best combination of cycling stability and capacity was demonstrated by the FeSnSb anode which was found to be composed of entwined nanocrystalline zones of SnSb and $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$. A reversible capacity of nearly 500 mAh g^{-1} was delivered by the FeSnSb anode for more than 120 cycles at a specific current of 0.05 A g^{-1} . Additionally, the FeSnSb anode outperformed the SnSb anode in the rate test as well.

Figure 6-6: (a) Galvanostatic charge-discharge of Fe-Sn-Sb alloys at 50 mA g^{-1} . (b) Rate performance of FeSnSb and SnSb.

A remarkable capacity of 200 mAh g^{-1} was attained by FeSnSb anode at 1 A g^{-1} while the SnSb anode failed when the current rate was increased. The improved rate performance of the FeSnSb anode when compared to pure SnSb anode could be attributed to the lower charge transfer resistance as observed from the electrochemical impedance spectroscopy measurements (Figure 6-7).

Figure 6-7: Electrochemical impedance spectroscopy of SnSb and FeSnSb alloy anodes.

The sodiation pathway and the structural evolution of the FeSnSb alloy was further investigated by cyclic voltammetry, ex situ XRD and HR-TEM analysis. As evident from the CV profiles in Figure 6-8a, the CV profiles of SnSb and FeSnSb have similar peak positions, suggesting similar reaction mechanism. The ex situ XRD patterns (Figure 6-8b) of the sodiated FeSnSb indicate presence of Na_3Sb and $\text{Na}_{15}\text{Sn}_4$ phases, similar to the sodiation reaction of SnSb.^{10, 11} Noticeably, $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ peaks were still present in the sodiated FeSnSb anode while the SnSb peaks almost vanished. The desodiated FeSnSb as well as the electrode after 120 cycles maintained the crystallinity and phase characteristics, further attesting the enhanced cycling performance.

Figure 6-8: (a) Cyclic voltammetry profiles of SnSb and FeSnSb. (b) Ex situ XRD profiles of FeSnSb at sodiated/de-sodiated stages.

The ex situ HR-TEM images and SAED patterns of the sodiated and the desodiated FeSnSb anode are presented in Figure 6-9. The sodiated FeSnSb anode exhibited lattice fringes and SAED patterns corresponding to the Na_3Sb and $\text{Na}_{15}\text{Sn}_4$ phases, attesting the XRD results. Moreover, $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ fringes were also observed in the sodiated anode, further confirming the inert behavior of the phase present in the FeSnSb alloy. During, the desodiation process, the FeSnSb alloy regained the initial crystalline structure as evident from the XRD pattern as well as the reappearance of the SnSb and $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ domains in the HR-TEM images and the SAED patterns. This further suggests the high reversibility and structural integrity of the unique microstructure of the FeSnSb anode obtained via melt-spinning process.

Figure 6-9: HR-TEM images and SAED pattern of (a-c) sodiated FeSnSb and (d-f) desodiated FeSnSb anode.

The $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ domains are expected to mitigate the induced stresses caused by the recurring sodiation/desodiation reactions in the anode. The schematic illustration (Figure 6-10) depicts the unique microstructure of FeSnSb mitigating the volume-expansion

induced stresses and maintaining the structural integrity of the electrode during the cycling process.

Figure 6-10: Schematic illustration of the sodiation/desodiation processes in the SnSb domains of FeSnSb alloy ribbon with the $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ domains buffering the induced stresses.

6.3.3 Sodium-ion battery full-cell performance evaluation

To further evaluate the suitability of FeSnSb anode for the practical applications, a full-cell study was carried out. NaVPO_4F cathode was chosen because of the high voltage of 3.4 V vs. Na as it can increase the energy density of the full-cell. The NaVPO_4F was synthesized by a previously reported protocol by Law *et al.*¹² Briefly, 1 mmol CTAB was dissolved in an ethanol-deionized water mixture (12:1 v/v). The solution was sonicated for 1.5 hrs. 4 mmol NaF, 4 mmol oxalic acid and 2 mmol V_2O_5 were added to the solution while stirring for half an hour. 4 mmol $\text{NH}_4\text{H}_2\text{PO}_4$ was added to the solution and continued stirring for a day. Later, the solvent was evaporated, and the residue was ground in a mortar and pestle. The powder was then annealed in Argon atmosphere at 800 °C for five hours to obtain the NaVPO_4F cathode material. The cathode was fabricated with aluminum foil

as the current collector by slurry coating technique used for the anode fabrication. Prior to full-cell assembly, the FeSnSb anode was cycled in a Na half-cell for two cycles to mitigate the irreversible capacity losses and ensure better cycling in full-cell configuration. The full-cell was then fabricated maintaining a 5:1 ratio of NVPF to FeSnSb to balance the capacity. The potential profiles of the anode, cathode and the full-cell are presented in Figure 6-11a. The average voltage for the FeSnSb anode is ~ 0.55 V vs. Na while for cathode it is ~ 3.4 V vs. Na. As a result, the full-cell has an average voltage of ~ 2.85 V with a capacity of ~ 300 mAh g⁻¹_{anode}. This corresponds to an energy density of ~ 826 Wh kg⁻¹ and the capacity was retained for over 25 cycles. Additionally, the full-cell exhibited moderate capacity of ~ 150 mAh g⁻¹ at a high current rate of 0.5 A g⁻¹. The preliminary full-cell results seem promising and further optimizations are expected to improve the cycling and rate performances.

Figure 6-11: NaVPO₄F/FeSnSb full-cell performance. (a) Potential profiles of the cathode, anode and the full-cell. (b) LED lamp powered by the full-cell. (c) Galvanostatic cycling performance. (d) Rate performance at different specific currents.

6.4 Conclusion

In conclusion, the ternary Fe-Sn-Sb alloy with characteristic microstructure was found to alleviate the issues of cycling instability by mitigating the induced stresses upon sodiation/desodiation reactions. The sodiation mechanism and the phase and structural evolution during sodiation/desodiation reactions was investigated. The potential of the ternary anode in a full-cell configuration was also investigated. The outstanding results exhort the potentials of microstructural engineering of alloying anodes to enhance the cycling stability for sodium-ion batteries.

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Chapter 7

Design and synthesis of FeSbO₄ nanoparticles: investigating sodium storage pathways and electrochemical performance for sodium-ion battery

In this study, a facile and scalable synthesis protocol was designed to obtain FeSbO₄ nanoparticles with high phase purity. The morphology and structural features of the nanoparticles were characterized. The electrochemical performance of the FeSbO₄ anode was investigated and the phenomenon of electrochemically induced amorphization was revealed via operando XRD investigations. Additionally, the sodium storage pathways were unveiled via voltammetry and spectroscopic investigations. Furthermore, the practical utility of the anode was explored in full-cell sodium-ion battery configuration with NaVPO₄F cathode delivering high energy densities.

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7.1 Introduction

A combination of alloying and conversion reaction mechanisms in sodium-ion batteries is considered as a strategic approach to obtain lower sodiation/desodiation voltages as well as improved reaction efficiency.¹⁻³ In this context, rutile-type metal oxide FeSbO₄, also known as Tripuhyite, can deliver a theoretical capacity of 1220 mAh g⁻¹ upon full conversion and alloying reactions with sodium hypothesizing the following reactions:⁴

However, in the early 1990s while FeSbO₄ was investigated for its catalytic performances, the electrochemical performance of FeSbO₄ has not been explored in detail.⁵⁻⁷ Recently, the lithium storage performance of FeSbO₄ was explored by Zeng *et al.* and a reversible capacity of only 107 mAh g⁻¹ could be achieved due to the pulverization of the microparticles and the incomplete lithiation reactions.⁴

Nanostructured materials provide efficient pathways for the electrochemical reactions as well as tolerate the stresses induced during the alkali-ion storage.⁸ Moreover, the nanostructuring of active material can promote faster diffusion of larger sized Na⁺ ions enabling better rate performance. In this study, a facile and scalable synthesis protocol is designed to yield nanoparticles of FeSbO₄ and the electrochemical properties of the nanoparticles are investigated. The sodium-storage mechanism in FeSbO₄ nanoparticles is elucidated and the preliminary full-cell study of NaVPO₄F cathode and FeSbO₄ anode is carried out.

7.2 Experimental methods

7.2.1 Material synthesis

Synthesis of FeSbO₄ nanocrystals: Iron (III) acetate (Sigma-Aldrich) and antimony (III) acetate (Sigma-Aldrich) were mixed in a 1:1 stoichiometric ratio (1 mmol each) in ethanol (20 ml) and the mixture was stirred for 2 h. Then, polyvinylpyrrolidone (MW=1,000,000, Sigma-Aldrich; 2 g) was added to the solution and stirred overnight. The viscous solution was then transferred to an alumina crucible and calcined in air at 1000 °C at a heating rate of 5 °C per minute to obtain the FeSbO₄ powder.

The NaVPO₄F cathode material for the full-cell study was synthesized according to a previous report.⁴² Briefly, hexadecyltrimethylammonium bromide (CTAB, Alfa Aesar, 1 mmol, 0.36445 g) was added to a beaker containing ethanol (12 ml) and deionized water (1 ml). The solution was then sonicated for 1.5 h. NaF (Sigma-Aldrich, 4 mmol, 0.16795 g), oxalic acid (Sigma-Aldrich, 4 mmol, 0.36012 g) and V₂O₅ (Sigma-Aldrich, 2 mmol, 0.36376 g) were sequentially added to the solution, which was then stirred for 30 min. Subsequently, NH₄H₂PO₄ (Sigma-Aldrich, 4 mmol, 0.46012 g) was added to the solution, which was then stirred for 24 h. After the solvent was evaporated, the residual powder was ground using a mortar and pestle, and pelletized. The pellet was then fired in an Argon tube furnace at 800 °C for 6 h to obtain the NaVPO₄F phase.

7.2.2 Materials characterization

Powder X-ray diffraction was carried out by using a Bruker D8 Advance diffractometer with a CuK α radiation source ($\lambda=0.15418$ nm). STEM imaging was performed with a state-of-the-art aberration-corrected JEOL JEM-ARM200F microscope. The accelerating voltage was 200 kV, the convergence angle was approximately 30 mrad, and the HAADF detector settings ranged from 68 to 280 mrad. HR-TEM images were obtained by using a JEM-2100 apparatus (JEOL) with an accelerating voltage of 200 kV. The SAED patterns were recorded by adding an intermediate lens aperture with a diameter of 20 mm. Operando X-ray diffraction studies were carried out on a Rigaku SmartLab X-ray diffractometer (200 mA, 45 kV) in reflection mode, with copper (1.54 Å) as the X-ray source, using a cell that

was developed in-house (**Figure S13**). XPS measurements were performed using a PHI-5400 apparatus with an Al K α beam source (250 W) and a position-sensitive detector. For HR-TEM and XPS measurements, the samples were sealed under an argon atmosphere and transferred to the chamber to minimize exposure to ambient air.

7.2.3 Electrochemical characterization

Electrochemical testing was carried out by using CR2016 coin cell assemblies. The electrodes were fabricated with FeSbO₄/Super P carbon (Timcal)/carboxymethyl cellulose (Sigma-Aldrich) in a 8:1:1 ratio, stirred overnight in deionized water, cast on copper foil, and dried in air at ~60 °C for 12 hours. The electrodes were punched out as 14 mm disks with ~2 mg cm⁻² active material loading and dried overnight at 100 °C in a vacuum oven prior to coin cell assembly. For the full-cell testing, FeSbO₄ anode was cycled in Li/Na half-cell configuration for few cycles to assist the initial SEI formation and lower the irreversible capacity losses in the full cells. For the operando XRD studies, FeSbO₄, Super P carbon and teflonized acetylene black (8:1:1 w/w/w) were mixed and pressed onto a 20 mm diameter stainless steel mesh (0.25 mm thickness, Good Fellow). Coin cells were assembled in an argon-filled glovebox (MBRAUN) with oxygen and water content of less than 1 ppm, and 1 M LiPF₆ in ethylene carbonate/diethyl carbonate/fluoroethylene carbonate (EC/DEC/FEC, 45:45:10 v/v/v) electrolyte and lithium metal counter electrode were used for LIB performance evaluation, while 1 M NaClO₄ (Sigma-Aldrich) in ethylene carbonate, propylene carbonate and fluoroethylene carbonate (EC/PC/FEC 45:45:10 v/v/v; Sigma-Aldrich) electrolyte, and a sodium metal (Sigma-Aldrich) counter electrode were used for sodium-ion battery testing. A porous glass-fiber separator (Whatman cat. number: 1825-04712) was used as the separator. A Solartron 1470E electrochemical workstation was used for the cyclic voltammetry measurements. Galvanostatic cycling tests were carried out by using a Neware multi-channel battery-testing system. A BioLogic SP-300 potentiostat/galvanostat was used to cycle the electrochemical cell for operando X-ray diffraction studies.

7.2.4 STEM image simulation

STEM HAADF image simulations were performed using a QSTEM simulation package, which employed the FFT multislice algorithm with frozen phonon configurations. The convergence angle, detector settings, and all other parameters (such as aberrations) matched those in the experimental conditions.

7.3 Results and discussion

7.3.1 Synthesis of FeSbO₄ nanoparticles

Nanosized FeSbO₄ particles were synthesized following a polyvinylpyrrolidone (PVP) assisted technique as illustrated in Figure 7-1. The PVP plays the role of stabilizer, size control agent and dispersant to assist the synthesis of FeSbO₄ nanoparticles.⁹ Briefly, the iron and antimony acetates were stirred in the aqueous PVP solution for two hours and then calcined in a box furnace at 1000 °C to get phase-pure FeSbO₄ nanoparticles.^{10, 11}

Figure 7-1: Schematic illustration of the synthesis of FeSbO₄ nanoparticles.

The phase-purity of FeSbO₄ was highest at calcination temperature of 1000 °C when compared to the phases formed at lower temperatures of 600 and 800 degrees. Moreover,

the weight percentage of PVP was optimized as 2g per 20 ml of the solution to produce uniformly dispersed FeSbO₄ nanoparticles as seen in Figure 7-2.

Figure 7-2: (a) Phase-purity of FeSbO₄ according to the calcination temperature. Variation of the particle size and distribution according to the amount of PVP. (a) 0 g mL⁻¹ (b) 0.05 g mL⁻¹ (c) 0.1 g mL⁻¹.

7.3.2 Structural and morphological characterization

The Rietveld-refined XRD pattern of the FeSbO₄ nanoparticles is presented in Figure 7-3a. The high crystallinity of the FeSbO₄ powder is attested by the sharp and intense diffraction pattern. The phase is consistent with the $P42/mnm$ rutile structure.¹² Atomic scale imaging by means of scanning transmission electron microscopy (STEM) enabled direct visualization of the crystal structure of FeSbO₄ nanoparticles (Figure 7-3b, c).¹³ Additionally, Figure 7-3c provides further evidence of the high crystallinity of the FeSbO₄ nanoparticles. As the imaging was carried out near the edge of the particle, a gradual

change in contrast due to thickness variation is observed. The overlay of the atoms agrees perfectly with the experimental STEM image as seen in Figure 7-3d as well as with the simulated STEM image presented in Figure 7-3e and model crystal structures presented in Figure 7-3f, g in the $[3\bar{1}\bar{1}]$ viewing direction.

Figure 7-3: (a) XRD pattern of FeSbO₄ nanoparticles. STEM image at (b) low magnification (c, d) high magnification. (e) Simulated STEM image (f, g) Model crystal structure in $[3\bar{1}\bar{1}]$ viewing direction.

Furthermore, the morphology of the FeSbO₄ particles was investigated by HR-TEM as presented in Figure 7-4. Multi-faceted polyhedral-shaped particles of ~40-80 nm size are observed. A magnified view (Figure 7-4b) indicated the lattice fringes corresponding to the d-spacing value of 0.328 nm of (110) plane of the FeSbO₄ phase. Additionally, the SAED pattern (Figure 7-4c) could also be indexed to the rutile-FeSbO₄ phase.

Figure 7-4: (a) HR-TEM image of FeSbO₄ nanoparticles. (b) Lattice fringes corresponding to the (110) d-spacing. (c) SAED pattern.

7.3.3 Electrochemical performance of FeSbO₄ in sodium-ion half-cell configuration

The cyclic voltammogram of FeSbO₄ vs. Na is presented in Figure 7-5a. The initial sodiation of FeSbO₄ showed a peak close to ~0.3 V vs. Na which is due to the electrolyte reduction and SEI formation as well as the structural transformations accompanying the conversion reactions at the anode.^{14, 15} From the second cycle onwards, a broad reduction peak is observed at ~0.5 V vs. Na, corresponding to the alloying reaction to form Na₃Sb. The desodiation peaks at ~0.84 and ~1.34 V vs. Na corresponds to the dealloying reaction and the oxidation reactions respectively.¹⁶ The galvanostatic cycling results indicate the good stability of FeSbO₄ anode at a specific current of 0.05 A g⁻¹. The initial sodiation capacity was close to 700 mAh g⁻¹ and stabilized close to 400 mAh g⁻¹, corresponding to 3 moles of sodium, from the second cycle. Moreover, the rate tests indicated the ability of the anode to endure high current performance as a moderate capacity of ~100 mAh g⁻¹ was achieved at high current of 1 A g⁻¹. The potential profiles also conform to the redox peaks observed in the voltammograms with a sloping plateau, common for nanostructured conversion materials.

Figure 7-5: Electrochemical performance of FeSbO₄ anode in sodium-ion half-cell configuration (a) Cyclic voltammogram (b) Galvanostatic cycling at 0.05 A g⁻¹ (c) Rate test (d) Potential profiles.

7.3.4 Phase transformation, structural and morphological evolution of FeSbO₄ during sodium storage

The phase and structural/morphological transformations in FeSbO₄ nanoparticles were investigated by in situ XRD and ex situ HR-TEM analyses.

7.3.4.1 Operando XRD investigation

Operando XRD facilitates the visualization of the phase changes in FeSbO₄ during the sodiation/desodiation processes as and when they occur. As seen from Figure 7-6, the (110) peaks at $\sim 2\theta = 27^\circ$ shift by $\sim 0.054^\circ$ during the initial Na insertion and the sharp peaks including (101) reflection completely disappeared during the sodium extraction from FeSbO₄ nanoparticles. Moreover, the Bragg reflections did not reappear after the extraction of the sodium ions during complete desodiation, suggesting electrochemically induced

solid state amorphization of FeSbO₄ nanoparticles. This amorphization is a precedent to the conversion reaction as also observed by Limthongkul *et al.* in the Li-Si system due to the thermodynamic limitations to manifest the transitional phases during the conversion reaction.¹⁷ Thus, the operando XRD revealed the electrochemically induced amorphization in FeSbO₄ anode upon the conversion reactions for sodium storage. However, due to the amorphization process, the phase changes in FeSbO₄ could not be further probed by XRD but by spectroscopic methods.

Figure 7-6: Operando XRD profiles during the sodiation/desodiation of FeSbO₄ nanoparticles.

7.3.4.2 Ex situ HR-TEM investigation

The morphological changes in FeSbO₄ upon sodiation reaction was probed by HR-TEM. Upon investigation, the sodiated FeSbO₄ particle (Figure 7-7a) appears volumetrically expanded and the diffuse rings in the SAED pattern (Figure 7-7c) suggest amorphization of the particles.^{18, 19} This observation further confirms the electrochemically induced solid

state amorphization process in FeSbO₄ upon sodiation reaction. Moreover, ~12 nm thick SEI layer was observed on the surface of the particles (Figure 7-7b). This could explain the initial irreversible capacity loss during sodiation reactions of FeSbO₄ anode.

Figure 7-7: HR-TEM investigation of sodiated FeSbO₄ nanoparticles. (a) Volume expansion upon sodium storage. (b) SEI formation on the nanoparticle surface. (c) SAED pattern.

7.3.5 Sodium storage pathways in FeSbO₄

Owing to the amorphization process, the reaction pathway could not be identified by means of XRD technique. Hence, ex situ XPS was employed to identify the reaction route adopted by the FeSbO₄ conversion anode. The survey spectrum of the pristine FeSbO₄ powder is presented in the Figure 7-8a. The Sb 3d and Fe 2p peaks are shown in the inset, with binding energies corresponding to the pentavalent and trivalent states of Sb and Fe respectively.²⁰ Sb 3d peaks can be used to gauge the chemical-state transitions during the conversion reactions on FeSbO₄ anode. The Sb3d_{5/2} doublet peak shifted ~0.3 eV upon sodiation of FeSbO₄ as depicted in Figure 7-8b. This suggests a transition from Sb⁵⁺ to Sb³⁺ indicating the formation of Sb₂O₄ which has Sb in the mixed valence states.^{21,22} The alloying reaction to form Na₃Sb is confirmed by the broad peak at ~536 eV.^{23,24} However, the experimental capacity achieved suggests reversible storage of three moles of sodium, indicating the reversible alloying reaction to proceed after the initial sodiation. Hence the sodiation mechanism could be explained as:

Initial sodiation of FeSbO₄:

Subsequent sodiation/desodiation reactions :

Figure 7-8: XPS analysis (a) Survey spectrum of pristine FeSbO₄ powder. (b) Sb 3d peak analysis of sodiated/desodiated FeSbO₄. (c) Schematic illustration of the structural and morphological evolution of FeSbO₄ upon sodium storage.

Furthermore, the kinetics of the sodium storage in FeSbO₄ was investigated by cyclic voltammetry measurements at increasing voltage scan rates. As the scan rate was increased from 0.1-2 mV s⁻¹, significant peak shift and increase in peak current was observed. Employing the power law, peak current was plotted according to the following equation:

$$\log i_p = b \log v + \log a$$

where, a and b are constants, i_p is the peak current, v is the scan rate.

A '*b*' value of 1 indicates surface controlled/pseudocapacitive regime while a value of 0.5 specifies a semi-infinite linear-diffusion-controlled regime.²⁵ For FeSbO₄ vs. Na, *b* value of 0.61 was observed and indicates dominance of diffusion-controlled behavior.

Figure 7-9: (a) Cyclic voltammograms of FeSbO₄ vs. Na at different scan rates. (b) Plot of log *i_p* vs. log *v*.

7.3.6 Investigation of FeSbO₄ anode in full-cell sodium-ion battery

To investigate the performance in a full-cell configuration, the FeSbO₄ anode was coupled with an NaVPO₄F cathode.²⁶ The full-cell could power two red LEDs as depicted in Figure 7-10b. The full-cell could deliver capacity close to 280 mAh g⁻¹_{anode} at an average voltage of 2.76 V corresponding to a high energy density of ~781 Wh kg⁻¹_{anode}. Further optimizations could improve the cycling stability of the full-cell, nevertheless, the high voltage and Coulombic efficiency are amongst the highest reported in literature.

Figure 7-10: Performance of NaVPO₄F/FeSbO₄ full-cell. (a) Schematic illustration of the sodium-ion shuttling in the full-cell. (b) LEDs powered by the full-cell. (c) Potential profiles. (d) Galvanostatic charge-discharge at 0.05 A g⁻¹.

7.4 Conclusions

In conclusion, a facile and scalable synthesis protocol was designed to synthesize FeSbO₄ nanoparticles of ~40-80 nm in size. The electrochemical performance was evaluated in half-cell and full-cell configurations. The electrochemically induced amorphization of FeSbO₄ nanoparticles was revealed by operando XRD measurements and the structural and morphological evolution was observed via ex situ TEM measurements. Moreover, sodiation pathway of FeSbO₄ anode was unveiled through cyclic voltammetry and ex situ XPS investigations. Preliminary full-cell investigations revealed high average voltage and Coulombic efficiencies, exhorting the potential of the conversion anode for high energy density sodium-ion batteries.

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Chapter 8

Conclusion and Future work

In this chapter, the major conclusions of the studies carried out are put into perspective and summarized. The novel contributions and findings are highlighted and compared to the statistics on alloying and conversion anodes for sodium-ion batteries from literature. The scope for future work and the possible strategies to further improve the performance of alloying and conversion anodes for sodium-ion batteries are discussed. These include the optimization and scale up of full-cell performance, material modifications and novel materials that warrant further investigations as sodium-ion battery anodes. The results and strategies could serve as a guideline and a diving board for further research into high-capacity sodium-storage materials.

8.1 Perspective

The aim of this thesis was to develop high-capacity anodes for sodium-ion batteries with good cycling stability and electrochemical performance. In this regard, the literature on SIB anodes developed so far was reviewed and alloying anodes based on Sn and Sb materials were found as ideal candidates in view of their low-cost, high sodiation capacities, suitable sodiation potentials, abundance and environmental safety. Additionally, the gaps in literature regarding the deployment of nanostructured materials and microstructural engineering of active materials for energy storage were identified and the problem statements were formulated to tackle these challenges.

In this work, Fe-Sn-Sb based alloying anodes were explored for their electrochemical performance in sodium-ion batteries. The sodiation mechanism was explored and various strategies were adopted to improve the cycling life of these alloying anodes. Additionally, preliminary studies were carried out in full-cell assemblies to gauge the practical utility of the developed anodes. A novel synthesis strategy was designed to fabricate FeSbO₄ nanoparticles and the electrochemical performance and sodiation mechanism was investigated. The study makes the case for the suitability of high capacity alloying and conversion anodes to enable the deployment of high energy density sodium-ion batteries for practical applications.

8.2 Summary of results

8.2.1 Investigating the carbon matrix induced performance of Sn-rich FeSn₂ alloy anodes for sodium-ion battery

- High-purity nanostructured FeSn₂ was synthesized through a facile solvothermal technique and the structural and morphological characterization of the material was carried out.

- The electrochemical performance and the sodiation mechanism of the alloying anode was investigated in half-cell configuration by means of cycling voltammetry and galvanostatic cycling tests.
- The cycling stability of the FeSn_2 anode was remarkably enhanced by utilizing FeSn_2 /Graphite composite anode fabricated by high-energy ball-milling process. The effect of graphite concentration on the electrochemical performance was optimized to achieve enhanced cycling stability.
- FeSn_2 /carbon composites were fabricated making use of three types of carbonaceous materials, namely, graphite, Super-P carbon and graphene and the cycling stability of the composites were investigated.

8.2.2 Synthesis of Sb-rich Fe-Sb alloy ribbons via melt-spinning process: investigation and performance evaluation as anodes for sodium-ion battery

- Fe-Sb alloy ribbons were fabricated via industrially viable melt-spinning process. The structural and morphological investigation of the alloy ribbons were carried out and the nanocrystalline features of the melt-spun alloy ribbons were revealed.
- The nanocrystalline features of the alloy ribbons translated into enhanced sodium-storage performance. The alloy ribbons delivered improved cycling stability and capacities when compared to bare Sb anode for sodium-ion batteries.
- The sodiation/desodiation mechanism of the alloy ribbons was investigated by means of cyclic voltammetry and ex situ XRD studies.
- The practical utility of the Fe-Sb alloy anode was further investigated in a full-cell configuration making use of sodium manganese oxide cathode. The full-cell delivered remarkable capacity and Coulombic efficiency, suggesting its practical utility.

8.2.3 Melt-spun ternary Fe-Sn-Sb alloys: tuning the microstructure to enhance the cycling stability for sodium-ion battery

- Novel ternary Fe-Sn-Sb anodes were synthesized via melt-spinning/rapid-solidification process for various concentrations of Fe. The structural and morphological characterization of the synthesized flakes were carried out.
- The Fe-Sn-Sb anodes outperformed the SnSb anodes in terms of cycling stability. The unique microstructure comprising of nanocrystalline domains in the ternary Fe-Sn-Sb alloy flakes buffered the stresses associated with the sodiation/desodiation reactions leading to enhanced cycling performance.
- The sodiation/desodiation behavior and the phase and morphological evolution of the Fe-Sn-Sb alloy flakes were investigated by ex situ TEM and XRD studies. The buffering of the stresses by the $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ during the sodiation/desodiation of the SnSb domains was revealed.
- The practical utility of the alloy flakes was gauged by designing a full-cell by coupling NaVPO_4F cathode to achieve high voltage. High capacities, Coulombic efficiencies and high energy density was achieved for the $\text{NaVPO}_4\text{F}/\text{FeSnSb}$ full-cell configuration.

8.2.4 Design and synthesis of FeSbO_4 nanoparticles: investigating sodium storage pathways and electrochemical performance for sodium-ion battery

- A novel route was designed to synthesize FeSbO_4 nanoparticles and the synthesis conditions were optimized to attain highest phase purity and nano-structuring.
- The electrochemical performance of the FeSbO_4 anode was investigated and the galvanostatic charge-discharge tests revealed the sodiation capacity and cycling stability of the anode.
- The sodium-storage behavior and the phase/structural evolution of the FeSbO_4 nanoparticles was evaluated by operando XRD, which revealed the electrochemically-induced amorphization of the nanoparticles upon sodium-ion storage.

- The morphological evolution and amorphization was further confirmed by ex situ HR-TEM investigations. The amorphous products were further examined by ex situ XPS to reveal the sodiation/desodiation mechanism of FeSbO_4 anode.
- The preliminary full-cell evaluation of FeSbO_4 anode and NaVPO_4F cathode showed high voltage full-cell with excellent capacity and Coulombic efficiency.

8.3 Novel contributions

- Employed facile and scalable high-energy ball milling method to fabricate FeSn_2 /Graphite composites and optimized the alloy-graphite ratio to achieve optimum sodium-storage performance and enhanced cycling stability.
- Synthesized Fe-Sb alloys via high-throughput, industrially-viable melt-spinning process. Investigated the electrochemical performance of the alloy anode in half-cell and full-cell sodium-ion battery configurations.
- Unveiled the unique microstructure of the ternary Fe-Sn-Sb alloy flakes synthesized by melt-spinning process and investigated the sodiation mechanism and structural/morphological evolution during sodium storage.
- Designed facile synthesis protocol for FeSbO_4 nanoparticles and revealed the electrochemically induced amorphization during sodium storage. The sodiation/desodiation mechanism as well as the morphological transformations of FeSbO_4 nanoparticles were revealed.

Figure 8-1: Comparison of electrochemical performance of the alloying-conversion anodes developed in this work to the reported intercalation-based anodes. (a) Half-cell configuration. (b) Full-cell configuration.¹⁻¹⁰

8.4 Future work

8.4.1 Optimization of full-cell performance

The preliminary full-cell investigations in this study seem promising as high capacities and Coulombic efficiencies were attained. However, the alloying and conversion anodes suffer from initial capacity loss due to the solid-electrolyte interphase formation as the conversion reactions. Consequently, the cathode to anode mass ratio must be optimized to improve the cycling stability of the full-cell.¹¹ Additionally, the anode should be pre-treated/pre-sodiated to alleviate these issues and hence future works aimed at minimizing the initial capacity loss in anode could benefit the optimization of full-cell performance. Moreover, the preliminary full-cell studies were carried out in coin-cell format. Further studies in pouch and cylindrical cells could provide meaningful metrics for evaluating the practical application of sodium-ion batteries making use of alloying and conversion-based anodes.¹²

8.4.2 All-active ternary/quaternary alloys

The use of all-active ternary and quaternary alloy materials could possibly enhance the sodium-storage capacity further and hence the energy density of sodium-ion batteries. In this regard, recently discovered sodium-alloying active materials such as Bi and Ge could be introduced to the Sn and Sb systems to further enhance the capacity and energy densities. Bi can form Na_3Bi leading to a theoretical capacity of 385 mAh g^{-1} while Ge forms NaGe delivering 369 mAh g^{-1} .¹³⁻¹⁸ However, the ratios of Sn-Sb-Bi-Ge should be optimized, and cost benefits of the ternary/quaternary alloys should also be taken into consideration to bring forth substantial impetus in this regard.

8.4.3 ABO_4 conversion anodes

While the present study focused on FeSbO_4 anode for sodium-ion batteries, the promising results call for further research into the ABO_4 class of materials. By varying the A and B cations, the sodiation pathway could be changed drastically and new mechanistic and reaction schemes could be investigated.^{19, 20} Computational calculations making use of density functional theory calculations could aid in the preliminary investigations as well.

8.5 Concluding remarks

In conclusion, the thesis titled “Investigation of tin and antimony based anodes with enhanced cycle life for sodium-ion batteries” successfully demonstrated the synthetic and engineering aspects to enhance the performance of alloying and conversion anodes for sodium-ion batteries. Scalable and industrially viable techniques were adopted to synthesize novel active materials for sodium-ion batteries. The sodiation/desodiation mechanism of the alloying and conversion anodes were elucidated and their performance was optimized in terms of good cycling stability. Moreover, preliminary investigations of the high capacity anodes in full-cell sodium-ion battery configurations were also carried out and demonstrated their feasibility for practical applications. The study provides an

impetus to future researchers and would open new avenues for research into alloying and conversion-based anodes for sodium-ion batteries.

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List of publications

1. **Edison, E.**; Satish, R.; Ling, W. C.; Bucher, N.; Aravindan, V.; Madhavi, S. Nanostructured intermetallic FeSn₂-carbonaceous composites as highly stable anode for Na-ion batteries. *Journal of Power Sources* 2017, 343, 296-302, DOI: 10.1016/j.jpowsour.2017.01.068.
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APPENDIX

Appendix A1 Comparison of electrochemical performance of recently reported SnSb anodes.

Material	Synthesis method	Capacity @ Specific current (voltage window vs. Na)	Cycles	Ref.
SnSb nanoparticles@3D-carbon matrix	Freeze-drying assisted solid-state method	~350 mAh g ⁻¹ @0.1 A g ⁻¹ (0.01-2 V)	100	1
Porous SnSb	Melt spinning and etching	~450 mAh g ⁻¹ @0.05 A g ⁻¹ (0.005-2 V)	100	2
Reduced graphene oxide incorporated SnSb@Carbon nanofiber matrix	Electrospinning	~490 mAh g ⁻¹ @ (0.01-2.5 V)	200	3
SnSb@3D N-doped porous graphene	Spray pyrolysis	~450 mAh g ⁻¹ @0.1 A g ⁻¹ (0.005-3 V)	100	4
SnSb@reduced graphene oxide@carbon microfibers	Centrifugal spinning	~350 mAh g ⁻¹ @0.05 A g ⁻¹ (0.01-2.5)	200	5
Fe-Sn-Sb alloy	Melt spinning	~500 mAh g ⁻¹ @0.05 A g ⁻¹ (0.005-2 V)	120	This work

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Appendix A2 Comparison of the FeSbO₄ anode with other sodium anodes reported in the literature.

Anode	Cathode	Voltage (V)	Capacity (mAh g ⁻¹)	Capacity retention	Initial coulombic efficiency	Reference
FeSbO₄	NaVPO₄F	2.75	283	55% (30 cycles)	93.7%	This work
Hard carbon	NaCrO ₂	2.8	260	100% (5 cycles)	78%	¹
Mo₃Sb₇	Na ₃ V ₂ (PO ₄) ₃	2	320	97% (20 cycles)	67%	²
SnS₂	Na ₃ V ₂ (PO ₄) ₃	1.6	375	53% (12 cycles)	66%	³
Bi₂S₃	Na ₃ V ₂ (PO ₄) ₃	1.7	340	84% (6 cycles)	71%	⁴
Na₂Ti₃O₇	Na _{2/3} Ni _{1/3} Mn _{2/3} O ₂	2.7	210	75% (100 cycles)	55%	⁵

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Appendix A3 Standardized Crystal Structure Data for FeSn₂ from ICDD database (Collection Code 247483)

Cell Parameters	a	6.5450
	b	6.5450
	c	5.3260
	a	90.000
	b	90.000
	g	90.000
Volume		228.15
Space Group		I 4/m c m
Formula Units per Cell		4
Crystal System		tetragonal
Laue Class		4/mmm
Crystal Class		4/mmm
Pearson Symbol		tI12
Wyckoff Sequence		h a
Calc Density		8.54
Structure Type		Al ₂ Cu
Axis Ratios	a/b	1.0000
	b/c	1.2289
	c/a	0.8138
Transformation Method		Tidy
Transformation Info		

Remark

EL	Lbl	OxState	WyckSymb	X	Y	Z	U	SOF
Fe	1	+0.00	4a	0.0000	0.0000	0.2500	0.0050	
Sn	1	+0.00	8h	0.1611	0.6611	0.0000	0.0056	

Appendix A4 Standardized Crystal Structure Data for FeSb₂ from ICDD database (Collection Code 186621)

Cell Parameters	a	5.8193
	b	6.5323
	c	3.2008
	a	90.000
	b	90.000
	g	90.000
Volume		121.67
Space Group		P n n m
Formula Units per Cell		2
Crystal System		orthorhombic
Laue Class		mmm
Crystal Class		mmm
Pearson Symbol		oP6
Wyckoff Sequence		g a
Calc Density		8.17
Structure Type		Marcasite-FeS2(oP6)
Axis Ratios	a/b	0.8909
	b/c	2.0408
	c/a	0.5500
Transformation Method		Tidy
Transformation Info		

Remark

EL	Lbl	OxState	WyckSymb	X	Y	Z	TF	SOF
Fe	1	+2.00	2a	0.0000	0.0000	0.0000		
Sb	1	-1.00	4g	0.1878	0.3565	0.0000		

Appendix A5 Standardized Crystal Structure Data for $\text{Fe}_{1.45}\text{Sn}_{0.5}\text{Sb}_{0.5}$ from ICDD database
(Collection Code 53536)

Cell Parameters	a	4.1800
	b	4.1800
	c	5.1900
	a	90.000
	b	90.000
	g	120.000
Volume		78.53
Space Group		P 63/m m c
Formula Units per Cell		2
Crystal System		hexagonal
Laue Class		6/mmm
Crystal Class		6/mmm
Pearson Symbol		hP5
Wyckoff Sequence		d c a
Calc Density		8.51
Structure Type		Ni ₃ SnP
Axis Ratios	a/b	1.0000
	b/c	0.8054
	c/a	1.2416
Transformation Method		Tidy
Transformation Info		Multiple transformations possible, first one selected

Remark

EL	Lbl	OxState	WyckSymb	X	Y	Z	TF	SOF
Fe	1	+0.00	2a	0.0000	0.0000	0.0000		0.7250
Fe	2	+0.00	2d	0.3333	0.6667	0.7500		0.7250
Sn	1	+0.00	2c	0.3333	0.6667	0.2500		0.5000
Sb	1	+0.00	2c	0.3333	0.6667	0.2500		0.5000

Appendix A6 Standardized Crystal Structure Data for FeSbO₄ from ICDD database (Collection Code 108879)

Cell Parameters	a	4.6388
	b	4.6388
	c	3.0773
	a	90.000
	b	90.000
	g	90.000
Volume		66.22
Space Group		P 42/m n m
Formula Units per Cell		1
Crystal System		tetragonal
Laue Class		4/mmm
Crystal Class		4/mmm
Pearson Symbol		tP6
Wyckoff Sequence		f a
Calc Density		6.06
Structure Type		Rutile-TiO ₂
Axis Ratios	a/b	1.0000
	b/c	1.5074
	c/a	0.6634
Transformation Method		Tidy
Transformation Info		

Remark

EL	Lbl	OxState	WyckSymb	X	Y	Z	TF	SOF
Fe	1	+3.00	2a	0.0000	0.0000	0.0000		0.5000
Sb	1	+5.00	2a	0.0000	0.0000	0.0000		0.5000
O	1	-2.00	4f	0.3150	0.3150	0.0000		