DISSERTATION

USING ELECTROCHEMICAL METHODS TO SYNTHESIZE AND UNDERSTAND ENERGY DENSE ANODES FOR LITHIUM-ION AND "BEYOND" BATTERY TECHNOLOGIES

Submitted by Jeffrey Ma Department of Chemistry

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Doctoral Committee:

Advisor: Amy L. Prieto

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ABSTRACT

USING ELECTROCHEMICAL METHODS TO SYNTHESIZE AND UNDERSTAND ENERGY DENSE ANODES FOR LITHIUM-ION AND "BEYOND" BATTERY TECHNOLOGIES

With the increasing occurrence of wildfires during summers and extreme blizzards during winters, society must look towards conversion into a renewable and carbon-free future to inhibit the growing problems caused by greenhouse emissions. An increased utilization of renewables such as geothermal, wind, and sunlight energy production has occurred in recent years as a response to those calls for change. However, the search for a way to store the energy produced from these sources for long term use during intermittent conditions is necessary. Due to advancements in Li-ion battery research during this past decade in conjunction with the decrease in their production cost, the utilization of batteries has evolved from primarily small portable devices to a broader range of applications in life. This includes its application as energy storage grids to support the expanding utilization of energy producing renewables in powering homes and businesses. Furthermore, the automotive industry is considering the permanent replacement of gas and combustion engines with battery powered electric motors. Batteries are this generation's catalyst for the next technological revolution towards a carbon free future. Among the parts in a battery cell, the battery anode is believed to be the next big step in improving the energy density of Li-ion and beyond technologies.

Herein, we describe investigations producing and improving the lifetime of potential anode materials for lithium-ion batteries and beyond. Specifically, our investigations herein will be focused on the electrodeposition of intermetallic alloy SnSb, designed to create higher energy dense and longer lifetime electrodeposited anode materials, and new electrochemical corrosion techniques to develop coatings for multivalent metals. In order to give clear context about the field

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of rechargeable battery chemistries, the first chapter of this dissertation is a brief review giving a perspective into current rechargeable batteries available in the market, current research, and current challenges in improving the current state-of-the-art lithium-ion batteries including work heading beyond lithium-ion technologies.

Chapter two details the successful electrodeposition of pure phase SnSb, by crystallinity, through the use of a deep eutectic ethaline solvent. The pure phase synthesis was developed through careful control of the ethaline solvent used, where humidity in the solvent was a factor that affected the pure-phase synthesis. This solvent acts as a double-edge sword, however, where overheating leads to the segregation of Sn ions from the solvent, resulting in Sb-rich products. These observations were collected through investigation of the electrodeposition products and through the use of different instrumentation to analyze the solution. The thin film performance as a lithium-ion anode was also investigated.

Chapter three describes the use of electrodeposited SnSb as thin-film sodium-ion anode. The lifetime and rate capability of the anode material in a sodium half-cell were reviewed. We herein also report the ex situ x-ray diffraction (XRD) study of the cycled material, showing the reformation of crystalline SnSb after continuous sodiation/desodiation process which has not been previously seen in a non-nanowire or single particle study. Comparison to the impure Sn rich production of this anode resulted in lower lifetime, showing the synergistic effect of SnSb reformation and the necessity in forming the pure phase SnSb.

Chapter four looks deeper into the SnSb sodiation process and identifies the reasoning for the significant capacity decrease with the increase of current rate. Electrochemical analysis through different methods such as the utilization of differential capacity plots and electrochemical impedance spectroscopy allows us to identify the rate limiting electrochemical event that causes less accessible capacity. The formation of a diffusion limiting phase is identified and discussed.

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Chapter five discusses the investigation into the aqueous electrodeposition of SnSb. Previous reports have utilized aqueous solvents to electrodeposit multi-crystalline Sn-Sb products, showing the complexity of the solvent and difficulties in creating 1:1 molar ratio SnSb. The effect of the pH of the electrodeposition solution on the resulting Sn-Sb product was investigated, revealing a range of compositions and morphology form depending on the solution conditions. Narrowing down to an ideal solution condition and further tuning the electrodeposition process resulted in a homogenous growth of SnSb throughout Ni foam.

Chapter six proposes different 3D architectural designs that can help enhance the stability and lifetime of electrodeposited 3D anodes. Specifically, the electropolymerization of porous polyaniline, which is needed in these different designs, has been carefully looked into. Different factors, such as acid concentration and the presence of light, were found to be important in initiating the polymerization of the aniline.

Chapter seven looks into the effect of single-walled carbon nanotube (SWCNT) and polyacrylonitrile (PAN) additives on enhancing SnSb composite lithium-ion batteries. SWCNT increases the mechanical stability of intermetallic alloys while PAN increases surface stability by encapsulating the volume changing active material. The cyclization of PAN further increased the mechanical effectiveness of the coating, but was identified to be a limiting factor in high current rate capabilities.

Chapter eight discusses the use of electrochemical corrosion in the search for ionically conductive coatings. The electrochemical corrosion of Mg₃(PO₄)₂ coating on Mg metal was investigated where careful control of the experimental parameters, including the use of applied voltage entry in this process, resulted in more control towards the homogenous growth of the coating.

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Chapter nine investigates utilizing a Ca-Sn coating to enhance the plating of Ca metal. Ca re-plating is only found to be stable in select electrolytes due to unstable interface formed in many common electrolytes that inhibit Ca-ion mobility. The preliminary experiments discussed in this chapter investigate how the coating may enable more stable plating and stripping in different solvents, showing the benefits of this coating.

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CHAPTER 1 – BEFORE, CURRENT, AND BEYOND – LITHIUM-ION BATTERIES – CHALLENGES AND PERSPECTIVE¹

1.1 Introduction

As advancements in technology continue to revolutionize society and change daily lives, the powering and application of these technologies continues to increase the total energy consumption required by society. Carbon based sources of energy (coal, oil, and gas) are still the dominant source of energy used in powering most homes.¹ However, renewables are no longer the lowest percentage of energy provided, and in the last 10 years have drastically increased to the point where they have now surpassed nuclear and biomass means of energy production. Nevertheless, the more environmentally friendly sources of energy are still less than half of the next highest source of energy, which is gas. Based on International Energy Agency's latest report, the global total energy supplied by renewables, nuclear, and biomass means in 2019 (2766 Mtoe) was still less than the lowest carbon energy source in the form of gas (3340 Mtoe). The main CO₂ emitting sources including gas, coal, and oil, continue to dominate the energy sector, and are expected to remain the main sources of energy for years to come.

Current CO₂ emissions are expected to increase in the upcoming years, as energy demands are projected to increase. Without any changes in sources of energy, carbon emissions will continue to grow and result in detrimental effects to different sectors of the environment in the future, including increasing temperature globally. Recent projections depict a drastic change in CO₂ emissions in the last year, due to the global economic shutdown from the COVID-19 pandemic, that resulted in the change in the CO₂ emission trajectory and a slowdown in the increase of CO₂ output.² This demonstrates current society's ability to reduce carbon emissions

¹ This chapter is written by Jeffrey Ma with guidance from Professor Amy L. Prieto. J.M. thanks Leslie Kraynak and Lily Moloney (Prieto Group, Colorado State University) for their writing suggestions for this chapter.

if people choose to limit their carbon emission sources. In recent years, the Paris climate agreement and other governmental policies around the world have been focused on reducing the climbing carbon emissions, with hopes to reduce emissions in the future.³ With the mixture of new governmental policies in the near future and the continued growth of energy and renewable infrastructure, the goal is to reduce carbon emissions to zero by 2100 if not earlier.⁴ The ability to reduce emissions will be solely dependent on society's willingness to adapt to newer renewable sources and progressive reform through government policies. The most recent projections for the US predicts the retirement of almost all coat plants by 2050, with renewables being the dominant source of energy in the U.S. by 2030.⁵ Without these policies, we will see an increase in the buildup of greenhouse gases, the weakening of the ozone and, ultimately, irreparable change with increased global temperatures.

One way to greatly reduce carbon emissions is to increase the production of renewable energy production sources. The presence of renewables, such as the rise of wind turbine farms and solar fields, have increased globally in the last 15 years. These energy production renewables have shown to be successful alternative to carbon sources, reduce reliance on an energy source only accessible by specific countries, while reducing overall cost and detrimental effects to the environment.⁵ However, these energy producing renewables have a great setback in which the production cannot be predicted to match the demand at different times of the day. Energy production by turbines is heavily reliant on the wind, while photovoltaic units are limited by the availability of the sun. In order to store the excess energy produced during times of successful energy production, all these energy production methods require some source of energy storage devices, such as batteries, are crucial for the storage of these energy production sources and allow for mobility of the source of energy. While the production of batteries has

recently been mainly focused on portable applications, the expansion of the use of batteries to other parts of life can help drive the successful conversion to a carbon free future.

1.1.1 Introduction to batteries and current battery technologies

The term "battery" was originally coined in the 1700s to describe linked capacitors used to transfer electricity but has been used in recent years to describe electrochemical cells used for energy storage. Batteries generally consists of two electrodes, the cathode and the anode, and an electrolyte that helps transfer ions to complete the balance reaction during the transformation of chemical energy into electricity. The cathode and anode are different materials that produce a chemical potential difference and are determined during the chemical work to release electricity, at which the cathode is chemically reduced, while the anode is chemically oxidized. Batteries are of interest in modern society as it allows for a more portable source of energy where the source of energy production. Batteries allow for the storage of electricity produced by renewable sources (nuclear, hydro, wind, solar, etc.), making renewable energies competitive against coal, fuel, and gas which makes reducing carbon emissions viable.

Typically, key traits of a good battery greatly relate to the size and weight of the battery. Depending on the battery desired, the material's storage and portability are crucial in its success for different applications. To analyze the electrical and physical performance of a battery, the energy density and power density of a material are crucial metrics. Energy density (in Watt-hour per kilogram or liter) is crucial for identifying the energy a battery can store for specific size and mass, while power density (in Watts per kilogram) is dependent on how quickly a material can deliver the energy. Other important traits for a successful commercial battery includes the cost to produce the battery, the lifetime of the battery, and the safety of operating the battery.

Batteries come in one-time-use (primary) forms of energy, or rechargeable (secondary) forms that allows for multiple use. Secondary batteries specifically, have expanded in recent years and are the key catalyst of major technological advancements ranging from laptops to smartphones to electric vehicles and more. The main types of batteries in the commercial secondary battery industry that build up most of the market's production and sales in current day technologies include lead-acid batteries, Ni-M batteries (where M stands for metal), and lithium-ion batteries. The history of different rechargeable batteries has been reviewed in other papers and will not be discussed here.⁶⁻⁸ However, the common rechargeable batteries found commercially will be briefly discussed to highlight the different chemistries that exist and are common at the point of this being written.

1.2 Different types of secondary batteries

1.2.1 Lead Acid Batteries

Lead acid batteries are currently the dominant secondary battery manufactured globally, and have the largest market share of all the rechargeable battery technologies in the market. Based on Grandview Research, lead acid batteries made up about 60% of the market in 2015.⁹ What makes lead acid batteries dominant currently is the reliability of these batteries. Lead acid batteries are commonly found in all parts of life, being used as starters for engines and powering transportation, ranging from wheelchairs to commuter trains, to being a source of backup power for buildings and grids.

Typically, lead-acid batteries consist of a lead (Pb) anode and a lead dioxide (PbO₂) cathode with a separator in between. The separator is filled with a concentrated acidic solution of sulfuric acid (H₂SO₄) that acts as the electrolyte that helps balance the chemistry of the battery during work. The following reaction occurs when work is being done via a lead acid battery:

Total reaction in the battery (forward reaction shown is when the battery is being discharged):

 $Pb_{(s)} + PbO_{2(s)} + 2 H_2SO_{4(aq)} \rightleftharpoons 2 PbSO_{4(s)} + 2 H_2O_{(l)}$

Process occurring at the cathode:

 $PbO_{2 (s)} + 3 H^{+}_{(aq)} + HSO_{4 (aq)} + 2 e^{-} \rightleftharpoons 2 H_{2}O_{(l)} + PbSO_{4 (s)}$

Process occurring at the anode:

 $Pb_{(s)} + HSO_{4(aq)} \rightleftharpoons PbSO_{4(s)} + H^{+}_{(aq)} + 2 e^{-1}$

The main benefits of lead acid batteries are its low cost and the battery's resilience to a wide range of conditions. Out of the different secondary battery technologies available commercially, lead acid batteries remain relatively low in cost, ranging from \$75 - \$150 per kWh.¹⁰ This type of battery also operates with a wide temperature range, from as cold as -30° C to as warm as 60° C. However, this battery is limited by its performance as a storage device due to its energy density. Lead acid batteries are limited to about 50 Wh kg⁻¹ of storage, resulting in large and heavy storage units of this form of battery. The batteries also have a limited lifetime of about 200 – 500 cycles, which is shorter than other available technologies. The Pb electrodes are also toxic to the environment and rises health concerns, leading to diligent handling and recycling protocols for these batteries.

1.2.2 Nickel – Metal batteries

Nickel metal batteries (Ni-M) are common rechargeable batteries commercially available mostly utilized for portable devices prior to the rise of Lithium-ion (Li-ion) technologies. The applications that Ni-M batteries are commonly used in range from radios and cameras to medical devices. The first generation of Ni-M batteries utilized Cadmium as the metal anode. But due to the expense and toxicity of cadmium, this metal was eventually replaced by Ni metal hydride (NiMH) technologies.

In current NiMH technologies, the battery consists of a nickel oxyhydroxide cathode, a potassium hydroxide electrolyte, and a metal hydride anode. The metal hydride used is typically

made of an intermetallic alloy. The following is the reaction that occurs when work is being done via a NiMH:

The total reaction in the battery (shown as the forward reaction when the battery is being discharged):

 $NiO(OH)_{(s)} + MH_{(s)} \rightleftharpoons Ni(OH)_{2 (s)} + M_{(s)}$

Process occurring at the cathode:

 $NiO(OH)_{(s)} + H_2O_{(l)} + e^- \rightleftharpoons Ni(OH)_2_{(s)} + OH^-_{(aq)}$

Process occurring at the anode:

 $MH_{(s)} + OH^{-}_{(aq)} \rightleftharpoons M_{(s)} + H_2O_{(l)} + e^{-}$

The main advantage of Ni-M batteries is the higher overall energy density this battery technology has compared to lead acid battery, while having similar resilience to a wide range of temperatures. Due to the lighter weight, portable technologies became more viable including the production of electric vehicles.¹¹ However, these batteries face problems with high discharge rate, decreasing capacity if not fully discharged, and high production cost. Due to Li-ion technology being better in every metric and the decrease of cost over time, Ni-M technology has been replaced by Li-ion in almost every major application. Ni-M batteries will further decrease in market share as the prices of Li-ion cells continue to decrease.

1.2.3 Lithium-ion batteries

Lithium-ion batteries are currently the most promising secondary battery technology that is driving the change towards green energy and enabling a renewable future. Every year lithiumion technologies continue to improve in performance, increase in production, and decrease in cost. While lead acid batteries still remain a large part of the industry, Li-ion batteries are expected to outgrow the pace in production of lead acid batteries, and are expected to overtake lead acid batteries to become the majority of secondary batteries produced by 2027.¹²

The Li-ion commercial battery typically consists of a lithium metal oxide cathode, a Li-based salt in carbonate solvent electrolyte, and a graphite anode. Using LiCoO₂ as the cathode, the following is an example of what typically occurs in a Li-ion battery:

The total reaction in the battery (showing the forward reaction when the battery is being discharged):

$$LiCoO_{2(s)} + C_{6(s, graphite)} \rightleftharpoons Li_{1-x}CoO_{2(s)} + Li_{x}C_{6(s)}$$

Process occurring at the cathode:

$$LiCoO_{2(s)} \rightleftharpoons Li_{1-x}CoO_{2(s)} + x Li^{+}_{(aq)} + e^{-x}$$

Process occurring at the anode:

$$C_{6 (s)} + x Li^{+}_{(aq)} + e^{-} \rightleftharpoons Li_{x}C_{6 (s)}$$

Lithium, being the most energy dense element in the periodic table, results in the highest energy dense storage material currently available to build batteries. However, due to the complexity of the Li-ion cell, every component of the battery contributes to both the advantages and the current disadvantages of the overall battery build. Some necessary improvements required in the Li-ion technology include increasing performance of the battery, increasing the safety of the battery, lowering the cost of the overall battery, and reducing the use of limitedsupply elements. The next section will focus more in-depth on the advantages and disadvantages of this technology, with a perspective of specific lithium-ion and "beyond Li-ion" related chemistry technologies. As this field has grown immensely – technologically over the last 30 years, through research, production, and economically of commercialization, the discussion on Li-ion battery as a topic requires a rich and diverse discussion in itself.

1.3 Lithium-ion batteries – Current chemistries

Lithium-ion battery (LIB) technologies have revolutionized society in the last 30 years by enabling a more mobile society. The successful implementation of smartphones, laptops, and other portable devices has been catalyzed by the commercialization of lithium-ion batteries. The biggest application that has led to an increased growth and advancement in LIBs in recent years is the emergence of electric vehicles (EV).

Although electric vehicles were first produced in the 1830s, the adaptation of electric vehicles was not widely accepted or adopted until this past decade.¹³ The advancement of LIBs from a specific energy of 90 Wh/kg, when it was first commercialized in the 1990s, to 220 Wh/kg today has enabled EVs to cover similar distances as internal-combustion engine vehicles (ICEV).¹⁴ The goal of the current automotive industry is to produce electric vehicles with a range of 400 miles, which is believed to be the about the range for ICEVs before the next fuel fill-up.¹⁵ The EV market, while still at its infancy, has overtaken portable devices as the biggest source of LIB demands. In the past decade, LIB production has increased about five-fold, from 25 GWh of cells produced in 2010 to about 125 GWh of cells produced in 2020.¹⁶ Due to this increase in production, the cost of LIBs has decreased from over \$1000/kWh in 2010 to below \$200/kWh today.¹⁷ Ultimately, the goal is for LIB to fall below \$100/kWh, which would make the batteries have a price equivalent to the average price of a gallon of gasoline.¹⁸ Current projections by BNEF believe this will occur by 2023.¹⁹

Over the last 30 years, the LIB chemistry has remained the same but batteries produced have shifted from the initial LiCoO₂/Graphite batteries to higher energy dense, faster charging, and safer materials.²⁰⁻²¹ Unlike other material science fields, the improvement of battery storage is not linear and is dependent on incremental improvement through better engineering of the current technology while we wait for the successful discovery and implementation of future chemistries. Nevertheless, the current incremental improvement of the LIB chemistry remains

bountiful and the technology still has many opportunities to grow. Current research towards the advancements in LIBs has been focused on tackling the following goals:

- Increasing the energy density of the overall LIB cell: both changes in the active and inactive components of the LIB cell can improve the energy density of current cells.
- Increase of power density of LIB cells: LIBs remain limited in their current chemistry with the rate electrodes can store and release electricity. Increasing power density can enable faster charging needed for EVs.
- Ways to reduce the cost: the current goal is to decrease the cost of LIBs to below the \$100/kWh threshold.
- Increasing safety of cells: if cells are abused current LIB are highly flammable and thermal runaway can occur. How can we reduce the dangers of LIB that contains a highly oxidizing material packed closely to a highly reducing material under pressurized conditions?

Of these main goals, the majority of lithium-ion battery research has been focused on the increase of energy density and how to lower cost without sacrificing lifetime and safety of the battery. The Department of Energy funded two different consortiums in the last 5 years to focus on such goals: Battery500 and Joint Centre for Energy Storage Research (JCESR). Battery500's focus was to decrease the battery cost below the \$200/kWh threshold. This consortium aims to increasing the energy density of the battery by replacing the current graphite technology used in current commercial cells, that has an energy density of 220 Wh/kg, with higher energy-dense materials and better electrolyte formulations. The goal is to increase the energy density of batteries to 500 Wh/kg. The advancement of lithium-metal anode technology and better control of lithium plating and stripping through advanced electrolyte systems have been focal points.²²⁻²⁶ JCESR had similar focus of developing a battery with a "555" promise – 5 times more energy, 5

times cheaper, in 5 years.²⁷ This goal aims for the improvement of battery technologies that would cost \$120/kWh. This consortium focused on the better understanding of new battery chemistries from the molecular level up and concentrated on all parts of the battery ranging from anode, cathode and electrolyte. JCESR is currently looking at chemistries beyond lithium-ion, and also includes non-traditional electrolyte formulations with the focus of safer and less flammable technologies. Ultimately, these consortia are looking to lower the price of batteries below \$100/kWh to enable the advancement of the EV market.

Even with these promising objectives towards battery advancements, many other factors still remain that greatly affect the success of lithium-ion batteries. Despite the successful identification of promising LIB materials that would increase the performance and lifetime of the overall LIB cell, the process for implementation and incorporation of the LIB technology into existing production lines remains a big limitation for the materials' transition from lab to market. Current production process of LIBs has been previously described in other papers, ranging from the considerations for producing precursors to the active materials for the battery and different steps for scaling up.²⁸⁻²⁹ Considerations must be made for the ease of technological transfer into existing production lines. Even prior to designing a scaled-up process for large scale production, work must be performed in identifying changes in the chemistry as the production scale of the materials increase. Furthermore, the chemistry must be better controlled as the process changes, and this optimization of production requires additional time and research. This huge investment of time, money, and effort is the main reason that limits the successful implementation of every promising LIB technology into the market.

Another factor that greatly affects the success of LIB in the future relates to the recycling and closing the loop of LIB production. As the amount of LIB produced increased drastically only in the last decade, questions about recycling of batteries have become a big concern. While LIB contain fewer toxic elements than other rechargeable batteries in the market, potential impacts

from incorrect disposal can still be a problem. Nevertheless, current LIB contains different components throughout the cell that are limited in availability around the world and recycling of the components will be necessary as less of the natural materials are available to mine. Recycling of LIB will look to recover most of the battery components, ranging in ways to recover and separate different metals to solvents. Current research working towards minimizing the energy throughout the recycling process is on the way and has been discussed in other papers.³⁰⁻³¹ Even prior to the recycling of the different components of the battery cell, some companies have recently announced plans of utilizing LIB in second life applications for energy grid storage after its end of life as a EV battery.³²⁻³³ Utilizing LIB to the fullest and minimizing the energy required to recycle and remake batteries will be crucial for the longevity of this technology for decades to come.

As we look for higher voltage LIB technologies to increase the energy density of lithium-ion, we push the materials in the battery to operate over their limits at conditions outside their windows of stability. This leads to both the performance benefits we desire and also stability issues throughout the LIB cell. These stability issues result in cell degradation and uncontrolled reactions observed at every interface, which requires further optimization via controlling the surface, electrolyte and electrode morphology to stabilize the cell. The focus on mitigating degradation is crucial, as better control of the degradation and instability can result in increasing the longevity of the cell, indirectly reducing the cost of replacing cells. The upcoming sections will discuss the current advancements and challenges identified for the different components of the lithium-ion battery in hopes to give a perspective of the different parts of in the LIB cell.

1.3.1 Anode – Current Technology and future perspective

Lithium-ion batteries have an interesting history of development, dating back to research in the 1970s by Exxon Mobil as an alternative source of energy during the US oil crisis.²¹ Initial lithium rechargeable batteries were developed and tested with lithium metal as an anode.

However, safety was revealed to be a huge challenge with this technology. Successive stripping and plating of Li metal resulted in uncontrolled dendritic growth on the anode. These dendrites can penetrate the separator resulting in high short-circuiting risks that can begin thermal runaway reactions and ultimately start a Li battery fire. This technology did end up in the market with the production of Li/MoS₂ lithium cells by Moli Energy, which were shortly recalled and its production ended due to several fire accidents. The following section describes the different benefits and challenges of currently commercial or researched Lithium-ion anodes.

1.3.1.1 Graphite and other carbonaceous materials

In order to design a safer lithium rechargeable technology, the concepts of using two intercalation hosts to shuttle and store Li ions were conceptualized, replacing the need for lithium metal.³⁴ The first reported lithium-ion intercalation candidate was studied in 1974, with a cyclic voltammetry study demonstrating that graphite can intercalate a variety of cations, including several different alkali ions like Li⁺.³⁵ However due to continuous co-intercalation of the common organic carbonate electrolyte used at the time, propylene carbonate (PC), into the graphite layers, graphite exfoliation was observed from the resulting volume change and stress. Ultimately this graphite exfoliation lessens the material's ability to store lithium and hinders the material's initial ability to reversibly be used. The first successful observation of lithium-ion reversible intercalation of graphite was observed using a solid electrolyte consisting of a polyethylene oxide and lithium perchlorate in 1983. Graphite remained unusable due to instability with electrolyte solvents of the time, resulting in the material's unavailability for commercial use until years later.³⁶ Before this discovery, the use of the carbonaceous material petroleum coke was developed and employed in the initial lithium-ion battery technology that was commercially released.²⁰ Petroleum coke is a lesser graphitized form of carbon that is able to reversibly store Li⁺ due to the amorphous regions of carbon that secures and brings together the different carbon layers.³⁷ The capacity of petroleum coke is limited compared to graphite (believed to be about 186 mAh/g or holding about $Li_{0.5}C_6$).

But, due to petroleum coke's ability to operate in PC, it was the first LIB anode. Successful reversible lithium intercalation of graphite in a lithium-ion battery cell did not occur until 1990, when liquid electrolyte formulation for LIB was improved with the introduction of ethylene carbonate (EC) as a co-solvent.

Since this discovery, carbon-based anodes have enabled Li-ion battery technology to grow in the commercial market and remains the dominant anode of choice for over 30 years. What makes graphite unique is the ability for Li ions to be stored between the layers of graphene planes. Theoretically, up to 1 Li atom can be stored per 6 Carbons in the graphite structure. This intercalation mechanism results in minimal volume change during Li-ion intercalation and deintercalation (about 10% volume change), resulting in 2D mechanical stability of the material and durability of this material for hundreds of cycles. This material is also electronically conductive and relatively low cost due to being made from an abundant source. Additionally, the material has higher energy densities compared to other intercalation anodes, with operating potentials between 0.05 V to 0.02 V vs Li/Li⁺. Graphite forms a stable solid electrolyte interface (SEI), a decomposition of the electrolyte onto the anode surface, during its initial cycle which remains stable after the initial formation. This has a huge effect on the battery's lifetime, as limited growth of the SEI and control of the SEI formation allows for a stable interface on the anode surface that allows Li ion mobility. Due to a combination of the material's low cost, moderate energy and power densities, and good cycle life, graphite has yet to be replaced. However, owing to the limited theoretical capacity (372 mAh/g) of graphite, the practical capacity of this material has been realized. In order to increase the energy density of LIB's, other materials must be investigated.

One way the commercial industry has increased the practical capacities of carbonaceous anodes is through the introduction of hard carbons. Hard carbons contain a mixture of small graphitic grains and are highly disordered, making them less likely to exfoliate when compared to graphite. Because of the disordered nature, the material is highly porous and contains voids that allow it to have reduced volume expansions upon lithium intercalation. In addition, these defects and voids from the disordered structure allow for excess gravimetric capacities by storage of Li ions in these voids and defects, resulting in a slight increase of practical capacity when compared to the theoretical capacity of graphite.³⁸⁻⁴⁰ However, due to the higher surface area of this material, the solid electrolyte interface (SEI) is more drastic when compared to graphite, resulting in a reduction of available Li in Li-ion full cells and ultimately a reduction of the capacity in a full cell.

Current research on carbonaceous anodes has been focused on increasing the energy and power density of these materials. Increase in power densities will allow for faster charging of EVs and enable LIB to be a competitive option compared to refueling at the gas pump. Graphite anodes, while able to handle moderate charging rates, encounter problems with lithium plating during fast charging due to the anode's low operating potentials close to Li plating and slow intercalation kinetics.⁴¹⁻⁴³ Research in recent years has investigated multiple different directions to increase power densities of carbonaceous anodes. To highlight a few, recent work has demonstrated the hybrid anode consisting of a graphite and hard carbon allowed successful access to fast charging capabilities.⁴⁴ Silicon oxide-carbon composites were also investigated for fast charging capabilities, where SiO_x coated graphite/graphene enabled faster Li diffusion into the graphite layers.⁴⁵⁻⁴⁶

In order to increase the energy density of carbonaceous anodes, research has recently been focused on the engineering and selected materials design. The energy density of graphite increases by calendaring graphite during electrode formation. Calendaring graphite increases the volumetric capacity of the material but may also result in mechanical grinding and the breakdown of graphite.⁴⁷ Another way to increase energy density of graphite is by using graphite-Silicon composites. Silicon anodes, which will be discussed in the next section, allow for access to higher energy densities and subsequently an increase in storage of the graphite anode composites

produced. This type of composite has recently begun being incorporated in commercial use for EVs and is viewed to be the next step of LIB cells.²⁸

1.3.1.2 Silicon and silicon oxide (SiOx) materials

Silicon anodes are considered one of the most promising materials due to their high energy density and abundance around the world. Silicon is the second most abundant element on earth and can be made by processing sand, resulting in a potential low cost for the material. Due silicon's ability to theoretically store 4.4 Li per silicon atom, silicon has the highest theoretical gravimetric capacity (4200 mAh/g based on Li_{4.4}Si) of all available Li-ion anode materials and has the highest overall energy density aside from Li metal itself. This promise of a relatively cheap material with a 10 times higher density has led to silicon anodes as the anticipated replacement for graphite in the next generation of commercial lithium-ion cells. However, silicon anodes face a challenge due to large volume changes with the incorporation of Li during battery operation.

Research on silicon as a lithium-ion anode dates back between 25 to 45. Silicon was found to lithiate in experiments dating back to 1976 but has yet to become a successfully commercialized anode material due to structural problems during lithium storage.⁴⁸ Unlike in graphite, where pre-formed layers exist to allow lithium ions to be intercalated with minimal volume change, lithium ion incorporation into a conversion intermetallic alloy like silicon results in excessive volume change and drastic change to the silicon anode structure as the battery charges and discharges. This results in a 320% change in size and a continuously pulverizing surface. The continuous pulverization of the surface results in continuous irreversible capacity loss from newly exposed surface that promotes additional electrolyte decomposition and solid electrolyte interface (SEI) formation. Unlike in graphite, where there is control of the SEI formation during the initial cycles, the continuous change that exposes new surface results in excessive SEI formation. This excessive SEI contributes to a drastic loss of lithium reserves in a full cell and a dense SEI layer that inhibits Li ion diffusion into the material.

Current research on the advancement of Silicon to commercialization varies greatly, with research focus ranging from better production of the material to enhancement of the material's cycle life through better control of its mechanical stability. In terms of production, silicon anode require careful handling under air free conditions, as oxidation of silicon occurs when exposed to air.⁴⁹ Harsh treatment, such as the use of HF, is required to remove the oxide layer if pure silicon is desired.⁵⁰ In terms of performance, silicon performance can be improved by limiting the material's expansion. Limiting operating potentials at which the Si lithiates minimizes volume expansion, resulting in less change on the surface SEI and a more stable passivating surface.⁵¹ Microstructuring of Si anodes, resulting in a more 3D morphology, helps alleviate the drastic volume change, although the higher surface area results in greater SEI growth.⁵²⁻⁵³ In recent years, the studies on controlled growth of SiO_x shell outside of silicon reveals that oxide shell to be beneficial to the lifetime of silicon anodes. While SiO_x has been shown to cause significant first cycle irreversible capacity loss due to the formation of an SEI containing Li₂O and Li₄SiO₄, this SEI was found to be beneficial to the anode overall, as it provides a more passivated surface.⁵⁴ The SEI formed on top of the thin SiO_x layer still allows for Li ion diffusion, while also restricting drastic volume expansion and the protection of Si within from further SEI growth.⁵⁵⁻⁵⁶ Solvent manipulation to alter the interface formed can further increase the capacity of silicon anodes.⁵⁷ Even so, the survivability of silicon anodes remains low and requires modest increase in lifetime for successful use in commercial applications.

In order to access the higher capacity of Si, small contents of Si have begun being incorporated to commercial graphite cells.²⁸ Amounts of about 2-10% silicon and SiO_x have been introduced into different silicon-graphite composite anodes for EV applications and have resulted in a modest increase in the overall capacity of the batteries. Based on the direction the battery industry is headed, silicon will continue to grow in its role of improving the capacity of current

commercial anodes. The extent of silicon's role will highly depend on the control of its structural and surface stability that ultimately correlates to the lifetime and safety of the cells produced.

1.3.2 Cathode – Current Technology and future prospective

Cathode materials have been a driving force for the successful application and advancements related to Lithium-ion batteries. The discovery of high voltage cathode materials catapulted the commercialization of LIBs and resulted in the dominance of this technology for portable applications. The LIB cathode consists of a metal oxide structure that allows for lithium intercalation. The history of cathode materials has been well documented previously by experts in the field.^{21, 58} The following sections will highlight important cathode structures and specific cathode materials that have an impact on modern and near future LIB technologies.

1.3.2.1 Layered oxides

Layered oxide cathodes have remained the main structure type of cathode material powering most commercial LIB cells since the technology's commercialization. The most notable discovery is the identification of LiCoO₂ by the Goodenough group. This in turn, resulted in the first intercalating layered cathode that was able to create a 4 V rechargeable battery.⁵⁹ This cathode material eventually became the cathode used by Sony in the first commercialized LIB and remains widely used in portable electronics today.⁶⁰ LiCoO₂ consists of alternating layers of octahedrally coordinated Li and Co with an array of cubic close packed oxide ions. The structure is the common O3 structure ordering that is commonly found in many layered-oxide cathodes. The naming of the layered oxide structures is discussed in an article by Delmas.⁶¹ What made LiCoO₂ (LCO) a very attractive material is its high theoretical capacity (274 mAh/g), high rate performance, and stable cycling. However, due to the overlapping of Co³⁺/Co⁴⁺ and O²⁻ 2p bands, oxygen evolution from the structure is favorable below Li_{0.5}CoO₂ during delithiation, resulting in only about 135 mAh/g of accessible reversible capacity before an irreversible structural change

occurs.⁶² LCO also requires the use of cobalt, an element with relatively low abundance, which results in the increase in cost relative to the increase in scarcity as production of cathodes goes up. In order to look for more thermally stable and relatively lower cost material with higher capacity, researchers have been investigating mixed metal oxide layered materials that have decreased amounts of cobalt.

In search of a lower Co content layered metal oxide cathode, incorporation of Ni and Mn as substitutes for Co has led to the successful discovery of LiNi_{1-y-2}Mn_yCo_zO₂ (NMC).⁶³⁻⁶⁴ NMC cathodes have become the most produced cathode due to the rise of EVs. The mixture of Ni, Mn, and Co results in a mixture of properties that allow for better chemical and structural stability, while increasing the energy and power density of the material. Cobalt in the layered structure has strong structural stability, but weak thermal and chemical stability. On the other hand, Mn has high chemical stability resulting in the full access of lithium without facing oxygen evolution, but faces structural instability, resulting in Mn migration into the Li layer and an eventual structural change.⁶⁵ Due to Ni's general middle ground relating to structural and chemical stability, advancements in NMC generally relates to the increase of Ni content. Common higher Ni content NMC (NMC higher than 111, where the Ni:Mn:Co ratio is 1:1:1) currently being researched includes 622 and 811 variants.⁶⁶ It is also worth mentioning that incorporation of Al is also observed to improve the thermal stability and electrochemical performance of the layered oxide.⁶⁷ LiNi_{0.8}CO_{0.15}Al_{0.05}O₂ (NCA), the resulting layered oxide, is commonly found in Tesla EV batteries.²⁸

These different Ni-rich layered oxides are promising as Ni allows for access to not only the redox state of Ni²⁺/Ni³⁺, but the material theoretically can access higher energy densities by accessing Ni⁴⁺. However, Ni⁴⁺ has been observed to cause a myriad of problems for high Ni content NMC at highly oxidizing potentials relating to cycling stability, thermal stability, and chemical reactivity.⁶⁸⁻⁶⁹ Specifically, at these higher potentials, oxygen evolution and the formation of rocksalt layer on the outer shell of Ni-rich NMC is noted. The rocksalt layer is found to cause a

higher impedance on the surface of the cathode and enables the rapid electrolyte oxidation on the cathode surface.⁷⁰⁻⁷³ This cathode electrolyte interface (CEI) formation, similar to SEI, increases impedance and resists Li-ion diffusion into the material.

Current research on these Ni-rich cathodes focuses on better understanding the process of failure at these higher potentials and how to mitigate the occurrence of the failure mechanism as well as CEI formation. Further clarity in identifying the mode of the rocksalt formation and oxygen evolution may help build a framework as to how these parameters react to cause the formation of the CEI. Recent work has identified the presence of singlet oxygen during the oxygen evolution.⁷⁴⁻⁷⁵ By tracking intermediate phases, like the singlet oxygen, the mechanism may become clearer and questions may be answered on whether the decomposition occurs on the surface of the electrode or in the electrolyte prior to appearing on the surface of cathodes. Other works have focused on resisting rocksalt formation and oxygen evolution by incorporating different gradient and core shell designs during the syntheses of the cathode.⁷⁶⁻⁷⁸ These design strategies will be crucial as we push to more oxidative potentials to increase the energy density of the battery. Even with the rise of Ni-rich cathodes, the rise in price and the limited availability of Co to specific regions of the world remain concerns.⁷⁹ The following section will discuss other works focused on Co-free cathodes.

1.3.3.1 Co-free cathodes

1.3.3.1.1 Spinel

LiMn₂O₄ (LMO) spinel cathodes are one of the earlier works focusing on replacing the LCO based cathodes.⁸⁰ The interest in LMO is due to the abundancy of manganese and the environmentally safe production of this manganese-based cathode. The LMO spinel structure consists of octahedral Mn and tetrahedrally coordinated Li in an array of cubic close pack oxygen. This results in a 4 V vs Li/Li⁺ cathode that allows for isotropic diffusion of Li ions in and out of the

material.⁸¹ However, similar to how Mn was discussed for NMC, LMO results in structural instability leading to low cyclability stemming from Mn dissolution into the electrolyte. The LMO instability results in an irreversible change of the structure to a tetragonal Li₂Mn₂O₄ rock salt phase.⁸² Mn dissolution is highly detrimental, as it not only permanently changes the structure of the cathode, but also affects the anode by forming an SEI that raises the anode impedance and resists Li diffusion into the anode.⁸³⁻⁸⁵ Nevertheless, LMO remains limited in its application due to the multiple levels of instability.

1.3.3.1.2 Cobalt-free layered oxide

Research on the different Li(Mn_xNi_{1-x})O₂ (NMO) cathodes can revolutionize the industry, as NMO can theoretically result in similar energy densities as LCO, but at a reduced cost. Advancements on NMO has improved the gravimetric capacity of the material to about 300 mAh/g, but slow rate capabilities are encountered for these materials.⁸⁶⁻⁸⁷ Similar to previous Mn containing cathodes, lifetime of the material remains a huge problem, as Mn dissolution and structural change continues to be a limiting factor to NMO cathode's capacity retention. Recently, LiNi_{1-x-y}Mn_xAl_yO₂ (NMA) cathodes have been reported, where the incorporation of Al is believed to suppress the Mn dissolution.⁸⁸ The successful Co-free layered oxide may appear in the future but requires better control of Mn stability for this to come true.

1.3.3.1.3 Phosphates

Phosphate based cathodes containing the olivine structure have been the most successful Co-free LIB cathode in the market. Since its discovery by the Goodenough group, the olivine LiFePO₄ (LFP) has been utilized in many portable applications ranging from home energy storage to e-cigarettes.⁸⁹ LFP is relatively low in cost, has good energy retention, low self-discharge, and fast rate capabilities.⁹⁰ Due to the lower operating potential of 3.4 V vs Li/Li⁺, LFP has a lower energy density when compared LCO, making it a questionable replacement. LFP intrinsically is

also a poor electronic conductor but this can be solved by the incorporation of a conductive coating to help promote Li ion diffusion.⁹¹⁻⁹³ Nevertheless, LFP is currently used as the general battery for Tesla model 3 produced in China.⁹⁴ Researchers have been looking into raising the energy density of phosphate olivine cathodes by investigating other transition metal and mixed transition metal phosphates. This type of research has led to promising materials such as LiCoPO₄, LiFe_{0.65}Mn_{0.35}PO₄, and Li₃V₂(PO₄)₃ to name a few.^{89, 95-97}

1.3.4 Electrolyte - Current Technology and future prospective

Electrolytes are the medium that allows for the movement of ions in an electrochemical system. However, as the anode and the cathode of a rechargeable battery begin to operate near the edges of the electrolyte stability window, the chemistry related to the electrolyte and its degradation can dictate the survivability of the cell. The electrolyte degradation at the surface of the electrode (depending on the electrode surface is called the SEI or CEI) dictates the diffusion of ions into the electrode and whether the growth of this layer continues. The ideal passivation of SEI or CEI on the electrode should be ionically conducting but electronically insulating. The electrolyte used in the LIB commercial industry typically consists of a lithium salt, either LiPF₆, LiBF₄, or LiClO₄, in an organic solvent that may contain ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and/or ethyl methyl carbonate (EMC). These solvent and salts are utilized due to their conductive properties and their ability to form favorable electrode-electrolyte interfaces with the current generation of LIB.

The electrolyte used in the first commercial LIB battery consisted of a propylene carbonate (PC) solvent. The PC solvent was found to intercalate into graphite resulting in the exfoliation of graphite layers due to the stress of the incorporation and the irreversibility of the anode. In order to enable the use of graphite as an anode, EC was introduced to the solvent, which was shown to suppress the degradation of the graphite layers due to the formation of a passivating SEI that stabilizes the graphite surface.⁹⁸ To further enable the use of EC with LCO, DMC was introduced

as an addition to EC to form a solvent mixture with LiPF₆ salt that had high ionic conductivity and improved oxidation stability enabling the use of 4.0 V vs Li/Li⁺ cathode materials.⁹⁹ This mixture of the cyclic EC with linear carbonates (DMC, EMC, DEC) containing LiPF₆ remains the most common formulation of electrolytes in today's commercial industry.²⁸ Cyclic carbonate additives such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC) are also commonly found to enhance the SEI passivation that is formed on LIB electrode surface.¹⁰⁰⁻¹⁰¹

In recent years, less viscous ester electrolyte solvents have been investigated in attempts to search for electrolyte formulations with higher conductivities. Esters, such as methyl acetate (MA), ethyl acetate (EA) and methyl formate (MF), were first studied to improve the carbonate solvents' performances at low temperatures.¹⁰²⁻¹⁰⁴ More recently, methyl butyrate (MB) and methyl propionate (MP) have been reported as solvents that have a wider temperature range stability than traditional carbonate solvents, illustrating that improved performance of cells utilizing these electrolytes resulted in better performance at the extreme ends.¹⁰⁵⁻¹⁰⁶ MA, MF, EA, MB, and MP have all been shown to improve conductivity of carbonate electrolyte mixtures, but the improvement is dependent on the amount of ester electrolyte solvent added.¹⁰⁷⁻¹⁰⁸ Too high content of ester solvents can negatively impact the SEI formed, resulting in reduced lifetime.¹⁰⁹

As LIB expands its role to new applications such as for use in EVs, the use of batteries for fast charging and the incorporation of new battery electrode materials result in the need for better formulation of electrolytes that will allow for controlled passivation of the electrodes at these new more extreme conditions. For example, most common carbonate electrolytes that are currently used allow good passivation for graphite anodes, but are identified to poorly passivate silicon anodes.¹¹⁰ Electrolytes also need to be able to increase in ionic mobility to allow for the high rate performance desired. As a result, current research looks for formulations that would not only create better passivation for new materials, but also increase in safety and performance. Most of the earlier electrolyte formulations previously mentioned focus on the solvent properties to

advance rate performance of the electrolyte use. In the conventional electrolytes mentioned above, salt concentration is typically close to 1 M to ensure sufficient solvent molecules can solvate around each cation and anion. In this scenario, solvent properties are crucial for Li-ion mobility.

In recent years, research has been more focused on understanding solvation of electrolytes to look for ways to advance the field. Researchers explored ways to alter the solvation sphere around the salt and solvent of electrolytes to increase the mobility of the Li-ion. The result of this search developed into the work on high concentration electrolytes (HCE).¹¹¹⁻¹¹² In HCE, high salt concentrations (> 3 M) are added into solvents so that no free solvent remains in the electrolyte and Li-ions are forced to share solvent molecules. As a result, this alternate type of solvation leads to aggregates of salt anions and Li cations that remain in close contact and promotes fast Li diffusion. Only a select number of salts can form these HCE, as the salt is required to have high solubility in solvents and high dissociation constant. Current Li salts that fit these criteria include lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium triflouromethanesulfonate (LiOTf), and lithium bis(pentafluoroethanesulfonyl)imide (LiBETI). On the other hand, a wide variety of solvents can be utilized for producing HCE.¹¹³⁻¹¹⁶ Interestingly, the SEI found in HCE has also been identified to be more inorganic rich due to the higher content of salt in the electrolyte, and may be aiding in the improved performance.¹¹⁶⁻¹¹⁷

Due to the high cost of Li salt to produce HCE, even more recent research has resulted in lower concentrations of Li salts used, while maintaining similar solvation structure found in HCE.¹¹⁸ This work, coined as localized high concentration electrolytes (LHCE), utilizes a diluent solvent that can mix homogeneously with the solvent used for HCE, while being insoluble for the salt. Recent work on LHCE demonstrates that a high performance electrolyte can be made while also utilizing a nonflammable solvent.¹¹⁹⁻¹²¹ Spun off of the concepts from HCE and LHCE, work on "water-in-salt" electrolyte has become a popular topic as this utilizes water as the solvent,

resulting in the use of a cheap and nonflammable solvent. Since the first report of "water-in-salt" electrolyte, the field has grown from not only expanding the electrochemical window of water to operating low voltage LIB cells, but being able to operate with in a 4 V LIB.¹²²⁻¹²⁴ The stability of the SEI formed from "water-in-salt" electrolytes still remains an issue, causing stability issues during cycling or resting.¹²⁵ Overall, further optimization in these types of electrolyte may lead to even better and safer electrolytes in the near future. However, the cost and safe handling of the new formulation of liquid electrolytes will remain the biggest barrier to replacing current LiPF₆ with carbonate solvent technology. Even with the successful formulation of an electrolyte that works well with the anode and cathode interfaces in the laboratory scale, the cost in scaling up, the simplification of the production process, and the incorporation into current production lines will remain the hinderance to its success for commercial use that will require much more time before it comes to fruition.

1.3.5 Separators, current collectors, and the remaining battery parts

While lab scale researchers calculate energy density based only on the active material, the full battery consists of cell casing, plastic, and other wiring that are required to build a successful battery pack. As we look to further increase the energy density of LIB cells for applications like EV and energy storage grids, some focus has been on maximizing the active components of the electrodes while minimizing the inactive parts of the cell. Current battery electrodes only make up for less than 30% of mass in a commercial LIB.²⁹ When looking at the cell level, 40% of the overall mass is due to the current collector. Electrode current collectors take up a huge portion of both mass and volume of the electrode. Recent research focuses on minimizing the percentage of the current collector in the overall cell by maximizing the thickness of active materials.¹²⁶⁻¹²⁷ Other inactive components, such as the separator, have also gotten thinner as the LIB technology improves.
Separators, typically made of plastics (such as polypropylene and polyolefin) have been engineered to be used as a line of defense for LIB safety. Separators are made not only to be filled with electrolyte, but also to act as a barrier between the cathode and anode to resist thermal runaway. However, as the thickness of the separator decreased, separators have become susceptible to punctures that lead to short circuiting, thermal runaway, and ultimately the danger of starting a fire. New materials for separators are currently being investigated to increase the safety of the cell from the materials design approach.¹²⁸ Companies have also looked into increasing the safety of separators by incorporating their own protective additive coatings that prevents punctures and mechanisms to suppress fires if thermal runaway occurs.

The lithium-ion battery may have looked the same over the last 30 years, but the understanding of the chemistry and the inner active and inactive components continues to change. This section highlights the many challenges and changes that the LIB has faced, and how with the advancement of new chemistries the rechargeable battery in the future will continue to change.

1.4 Beyond Li-ion technologies and alternatives

Lithium metal anodes have reemerged as the future anode material as it allows access to the highest energy density of all available lithium compatible anodes. Having the lowest electrochemical potential (-3.04 V vs standard hydrogen electrode) and a theoretical gravimetric capacity of 3860 mAh/g, it far surpasses all Li-ion anodes in accessible energy. However, the challenges that caused the unsuccessful commercialization of the lithium metal battery by Moli Energy in 1990s still remain, as the search to resist the uncontrolled growth of dendritic lithium during replating continues. Many different approaches to controlling lithium growth have been described elsewhere, including better control of interface through different coatings and electrolytes.¹²⁹ HCE and LHCE are promising for lithium metal anode technologies, as it promises

a nonflammable electrolyte and higher safety in the future.²⁴ Still, better growth of the interface on Li metal surface may be key to passivating Li and resisting dendritic growth.

Solid-state electrolytes have been of great interest due to the promise of a liquid free electrode that results in higher safety and enables the use of Li metal as an anode. Solid electrolytes are one of the main proponents that revitalized lithium metal research in the past decade. Ideally, solid-state electrolytes can inhibit Li dendrite growth, although current work on solid-state electrolytes indicates dendrites still exist and are still a problem that continues to plague and puncture solid-state electrolytes.¹³⁰⁻¹³⁶ Solid-state electrolytes that are currently being investigated can be divided into inorganic types, that can be further categorize into different structure types ranging from crystalline oxides, sulfides, argyrodites to glassy nitrides solids, and polymer type electrolytes.¹³⁷ Every type of solid-electrolyte still faces multiple issues ranging from electrochemical stability, chemical stability (reactive to humidity), mechanical stability (brittleness), to thermal stability (instability at very hot and very cold temperatures).¹³⁸ In addition, reactivity at the solid-solid interfaces between the solid-electrolyte and other components (anode and cathode) of the battery still remains a problem, so the solid-solid interface must be well designed and controllable.¹³⁹⁻¹⁴² While researchers working on this field are aggressively discovering new materials that can fulfill most properties, there is currently no perfect solid-state electrolyte material.

The success of solid-state electrolyte may enable some other beyond-Li technologies such as Li-S and Li-air.¹⁴³⁻¹⁴⁴ These technologies face interfacial issues and degradation in liquid electrolyte, which may be solved with the successful implementation of solid-state electrolyte.¹⁴⁵⁻¹⁴⁶ Even if an ideal solid-state electrolyte is discovered in the lab scale, the scalability, handling, and development of process to transfer this new technology into current manufacturing processes leave these technologies years away from being in the market.

Sodium- and Potassium- ion batteries (NIB and KIB, respectively) are good near future alternatives to alleviate the demands for LIB. Both Sodium and Potassium are more abundant than Lithium in the earth's crust, and their precursors are available more readily throughout the world at lower costs. While lower in cost and higher in abundance, the tradeoff in using NIB and KIB is the lower energy density than LIB. Due to the slightly lower energy densities, the successful commercialization of these technologies is expected to be applied as LIB alternatives in less energy density demanding applications, such as energy grid storage or even battery packs for short range electric vehicles. NIBs specifically, have been more extensively studied and are closer to being deployed commercially in upcoming years. Costs for NIBs are expected to be lower than LIBs not only due to the use of sodium, but also due to the top NIB cathodes currently available. To name a few, the top performing cathodes include layer oxide such as $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ and fluorophosphates such as $Na_3V_2(PO_4)_2F_3$ which are all Co-free cathodes and are drastically cheaper in cost compared to the Co containing LIB cathodes.¹⁴⁷⁻¹⁴⁸ However, many challenges remain for these alternative battery technologies including chemical reactivity issues and the large structural changes in these batteries. Due to the larger cation size of sodium and potassium, larger volume changes and structural instabilities are found during insertion and de-insertion into different electrodes.¹⁴⁹⁻¹⁵⁰ The larger cation also causes slower diffusion kinetics of the ions through the bulk solid electrodes. Problems remain in formulating good electrolytes for NIB and KIB. While most salts and solvents are transferred from LIB due to the belief that NIB and KIB are similar, the chemistry and reactivities of the electrolyte are found to be different in these alternative technologies. Specifically, lessons learned from LIB on passivation of surfaces are not directly transferrable.¹⁵¹⁻¹⁵² Higher reactivity of these traditional electrolyte formulations and higher solubility of the decomposing species results in a more unstable SEI in these systems.¹⁵³⁻¹⁵⁴ The search for different electrolyte formulations and additives is required to increase the stability and lifetime of these batteries.

Multivalent battery chemistries remain promising candidates to be in competition with LIB technology in the future due to high theoretical energy densities that may allow these chemistries to be applied into EVs.¹⁵⁵ Multivalent ions, such as Mg²⁺, Ca²⁺, Zn²⁺, and Al³⁺ all carry multiple charges per atom, resulting in higher volumetric capacities for these chemistries. These metals are all greater in abundance in the earth's crust, resulting in potentially lowered costs. All components of the battery remain a challenge in these chemistries. The materials discovery of multivalent cathodes remains limited and is necessary to enable the high theoretical energy densities of these chemistries.¹⁵⁶ For Ca and Mg batteries, their respective metals are utilized as the anode due to being the highest accessible capacity anode and the belief that no dendritic growth occurs during the replating of these metals.¹⁵⁷⁻¹⁵⁹ Research for Mg has revealed that dendrite formation still occurs at high enough currents and limits to the dendrite-free growth do exist.¹⁶⁰⁻¹⁶² Ca battery research is still very elementary due to the original belief, that lasted until the last few years, that replating was impossible for Ca metal.¹⁶³ Thanks to advancements in understanding of Mg metal passivation and electrolyte formulation, Ca chemistries have been revisited in recent years. The utilization of Ca electrolyte analogues has enabled the successful reversible plating and stripping of the Ca.¹⁶⁴⁻¹⁶⁷ Electrolytes that can access the electrochemistry of both the anode and cathode in these multivalent systems remain limited. Better control of surface passivation and discovery of easier accessible electrolyte formulations will be the next steps in moving these chemistries forward.

1.5 Conclusion

Highlighted in this chapter are some promising directions for Lithium-ion and other chemistries that may work alongside LIBs or even replace them. Lithium-ion batteries will be here to stay, as this technology is vital to our growing, energy-reliant society. Energy increases to LIBs will be unnoticeable as we slowly implement new designs and formulations that will come in small increments. While materials design may enable access to higher performance metrics,

understanding the interactions at the different interfaces is the key reoccurring point throughout the different technologies that will be critical in rising the safety and lifetime of the battery. Although it is unknown how long it will take for these "beyond Lithium-ion" chemistries to appear in the commercial market, it is promising to be able to identify these different approaches to providing a less carbon reliant society and moving towards a carbon-free future. One thing is known: batteries will continue to grow more energy dense, more powerful, last longer, be safer, lighter, and cheaper.

1.6 References

1. Global total primary energy demand by fuel, 2019. <u>https://www.iea.org/data-and-statistics/charts/global-total-primary-energy-demand-by-fuel-2019</u>.

2. Energy sector and industrial process CO2 emissions by recovery trajectory. https://www.iea.org/data-and-statistics/charts/energy-sector-and-industrial-process-co2emissions-by-recovery-trajectory.

3. Cai, Y.; Riezman, R.; Whalley, J., International trade and the negotiability of global climate change agreements. *Economic Modelling* **2013**, *33*, 421-427.

4. Energy and industrial process CO2 emissions and reduction levers in WEO 2020 scenarios, 2015-2030 <u>https://www.iea.org/data-and-statistics/charts/energy-and-industrial-process-co2-emissions-and-reduction-levers-in-weo-2020-scenarios-2015-2030</u>.

5. Annual Energy Outlook 2021. U.S. Energy Information Administration 2021.

6. Bonino, F.; Vincent, C. A., 6 - Secondary alkaline cells. In *Modern Batteries (Second Edition)*, Vincent, C. A.; Scrosati, B., Eds. Butterworth-Heinemann: Oxford, 1997; pp 162-197. 7. Schumm, B., Batteries. In *Encyclopedia of Physical Science and Technology (Third*

Edition), Meyers, R. A., Ed. Academic Press: New York, 2003; pp 57-75.

8. Scrosati, B., History of lithium batteries. *J Solid State Electrochem* **2011**, *15* (7), 1623-1630.

9. Battery Market Size, Share & Trends Analysis Report By Product (Lead Acid, Li-ion, Nickle Metal Hydride, Ni-cd), By Application (Automotive, Industrial, Portable), By Region, And Segment Forecasts, 2020 - 2027. <u>https://www.grandviewresearch.com/industry-analysis/battery-market</u>.

10. Cano, Z. P.; Banham, D.; Ye, S.; Hintennach, A.; Lu, J.; Fowler, M.; Chen, Z., Batteries and fuel cells for emerging electric vehicle markets. *Nature Energy* **2018**, *3* (4), 279-289.

11. German, J. M., Hybrid Electric Vehicles. In *Encyclopedia of Energy*, Cleveland, C. J., Ed. Elsevier: New York, 2004; pp 197-213.

12. Lithium-ion Battery Market Size, Share & Trends Analysis Report By Product (LCO, LFP, NCA, LMO, LTO, Lithium Nickel Manganese Cobalt), By Application, By Region, And Segment Forecasts, 2020 - 2027. <u>https://www.grandviewresearch.com/industry-analysis/lithium-ion-battery-market</u>.

13. Guarnieri, M. In *Looking back to electric cars*, 2012 Third IEEE HISTory of ELectrotechnology CONference (HISTELCON), 5-7 Sept. 2012; 2012; pp 1-6.

14. Placke, T.; Kloepsch, R.; Dühnen, S.; Winter, M., Lithium ion, lithium metal, and alternative rechargeable battery technologies: the odyssey for high energy density. *J Solid State Electrochem* **2017**, *21* (7), 1939-1964.

Barkenbus, J. N., Prospects for Electric Vehicles. *Sustainability* 2020, *12* (14), 5813.
 Ding, Y.; Cano, Z. P.; Yu, A.; Lu, J.; Chen, Z., Automotive Li-Ion Batteries: Current

Status and Future Perspectives. *Electrochemical Energy Reviews* 2019, 2(1), 1-28.

17. Nykvist, B.; Nilsson, M., Rapidly falling costs of battery packs for electric vehicles. *Nature Climate Change* **2015**, *5* (4), 329-332.

18. Trahey, L.; Brushett, F. R.; Balsara, N. P.; Ceder, G.; Cheng, L.; Chiang, Y.-M.; Hahn, N. T.; Ingram, B. J.; Minteer, S. D.; Moore, J. S.; Mueller, K. T.; Nazar, L. F.; Persson, K. A.; Siegel, D. J.; Xu, K.; Zavadil, K. R.; Srinivasan, V.; Crabtree, G. W., Energy storage emerging: A perspective from the Joint Center for Energy Storage Research. *Proceedings of the National Academy of Sciences* **2020**, *117* (23), 12550.

19. Henze, V. Battery Pack Prices Cited Below \$100/kWh for the First Time in 2020, While Market Average Sits at \$137/kWh. <u>https://about.bnef.com/blog/battery-pack-prices-cited-below-100-kwh-for-the-first-time-in-2020-while-market-average-sits-at-137-kwh/</u>.

20. Yoshino, A. S., K.; Nakajima, T. Secondary battery. JP patent 1989293 1985.

21. Whittingham, M. S., Lithium Batteries and Cathode Materials. *Chemical Reviews* **2004**, *104* (10), 4271-4302.

22. Zheng, Y.; Soto, F. A.; Ponce, V.; Seminario, J. M.; Cao, X.; Zhang, J.-G.; Balbuena, P. B., Localized high concentration electrolyte behavior near a lithium–metal anode surface. *J. Mater. Chem. A* **2019**, *7* (43), 25047-25055.

23. Xiao, J.; Li, Q.; Bi, Y.; Cai, M.; Dunn, B.; Glossmann, T.; Liu, J.; Osaka, T.; Sugiura, R.; Wu, B.; Yang, J.; Zhang, J.-G.; Whittingham, M. S., Understanding and applying coulombic efficiency in lithium metal batteries. *Nature Energy* **2020**, *5* (8), 561-568.

24. Perez Beltran, S.; Cao, X.; Zhang, J.-G.; Balbuena, P. B., Localized High Concentration Electrolytes for High Voltage Lithium–Metal Batteries: Correlation between the Electrolyte Composition and Its Reductive/Oxidative Stability. *Chem. Mater.* **2020**, *32* (14), 5973-5984.

25. Ren, X.; Gao, P.; Zou, L.; Jiao, S.; Cao, X.; Zhang, X.; Jia, H.; Engelhard, M. H.; Matthews, B. E.; Wu, H.; Lee, H.; Niu, C.; Wang, C.; Arey, B. W.; Xiao, J.; Liu, J.; Zhang, J.-G.; Xu, W., Role of inner solvation sheath within salt–solvent complexes in tailoring electrode/electrolyte interphases for lithium metal batteries. *Proceedings of the National Academy of Sciences* **2020**, *117* (46), 28603.

26. Čao, X.; Zou, L.; Matthews, B. E.; Zhang, L.; He, X.; Ren, X.; Engelhard, M. H.; Burton, S. D.; El-Khoury, P. Z.; Lim, H.-S.; Niu, C.; Lee, H.; Wang, C.; Arey, B. W.; Wang, C.; Xiao, J.; Liu, J.; Xu, W.; Zhang, J.-G., Optimization of fluorinated orthoformate based electrolytes for practical high-voltage lithium metal batteries. *Energy Storage Materials* **2021**, *34*, 76-84.

27. Yet-Ming Chiang, L. S., Mengshuan Sam Pan, and Zheng Li Lowering the Bar on Battery Cost. <u>https://www.cell.com/pb-assets/journals/research/joule/stories/battery-backstory/index.html</u>.

28. Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M., Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nature Energy* **2018**, *3* (4), 267-278.

29. Kwade, A.; Haselrieder, W.; Leithoff, R.; Modlinger, A.; Dietrich, F.; Droeder, K., Current status and challenges for automotive battery production technologies. *Nature Energy* **2018**, *3* (4), 290-300.

30. Harper, G.; Sommerville, R.; Kendrick, E.; Driscoll, L.; Slater, P.; Stolkin, R.; Walton, A.; Christensen, P.; Heidrich, O.; Lambert, S.; Abbott, A.; Ryder, K.; Gaines, L.; Anderson, P., Recycling lithium-ion batteries from electric vehicles. *Nature* **2019**, *575* (7781), 75-86.

31. Thompson, D. L.; Hartley, J. M.; Lambert, S. M.; Shiref, M.; Harper, G. D. J.; Kendrick, E.; Anderson, P.; Ryder, K. S.; Gaines, L.; Abbott, A. P., The importance of design in lithium ion battery recycling – a critical review. *Green Chemistry* **2020**, *22* (22), 7585-7603.

32. Casals, L. C.; Amante García, B.; Canal, C., Second life batteries lifespan: Rest of useful life and environmental analysis. *Journal of Environmental Management* **2019**, *232*, 354-363.

33. Kamath, D.; Arsenault, R.; Kim, H. C.; Anctil, A., Economic and Environmental Feasibility of Second-Life Lithium-Ion Batteries as Fast-Charging Energy Storage. *Environmental Science & Technology* **2020**, *54* (11), 6878-6887.

34. Armand, M. B., Intercalation Electrodes. In *Materials for Advanced Batteries*, Murphy, D. W.; Broadhead, J.; Steele, B. C. H., Eds. Springer US: Boston, MA, 1980; pp 145-161.

35. Besenhard, J. O.; Fritz, H. P., Cathodic reduction of graphite in organic solutions of alkali and NR4+ salts. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1974**, *53* (2), 329-333.

36. Yazami, R.; Touzain, P., A reversible graphite-lithium negative electrode for electrochemical generators. *J. Power Sources* **1983**, *9* (3), 365-371.

37. Winter, M.; Barnett, B.; Xu, K., Before Li Ion Batteries. *Chemical Reviews* **2018**, *118* (23), 11433-11456.

38. Dahn, J. R.; Zheng, T.; Liu, Y.; Xue, J. S., Mechanisms for Lithium Insertion in Carbonaceous Materials. *Science* **1995**, *270* (5236), 590.

39. Mukherjee, R.; Thomas, A. V.; Datta, D.; Singh, E.; Li, J.; Eksik, O.; Shenoy, V. B.; Koratkar, N., Defect-induced plating of lithium metal within porous graphene networks. *Nature Communications* **2014**, *5* (1), 3710.

40. Kaskhedikar, N. A.; Maier, J., Lithium Storage in Carbon Nanostructures. *Adv. Mater.* **2009**, *21* (25-26), 2664-2680.

41. Takami, N.; Satoh, A.; Hara, M.; Ohsaki, T., Structural and Kinetic Characterization of Lithium Intercalation into Carbon Anodes for Secondary Lithium Batteries. *J. Electrochem. Soc.* **1995**, *142* (2), 371-379.

42. Levi, M. D.; Aurbach, D., Diffusion Coefficients of Lithium Ions during Intercalation into Graphite Derived from the Simultaneous Measurements and Modeling of Electrochemical Impedance and Potentiostatic Intermittent Titration Characteristics of Thin Graphite Electrodes. *The Journal of Physical Chemistry B* **1997**, *101* (23), 4641-4647.

43. **!!! INVALID CITATION !!!** {}.

44. Chen, K.-H.; Goel, V.; Namkoong, M. J.; Wied, M.; Müller, S.; Wood, V.; Sakamoto, J.; Thornton, K.; Dasgupta, N. P., Enabling 6C Fast Charging of Li-Ion Batteries with Graphite/Hard Carbon Hybrid Anodes. *Advanced Energy Materials* **2021**, *11* (5), 2003336.

45. Kim, N.; Chae, S.; Ma, J.; Ko, M.; Cho, J., Fast-charging high-energy lithium-ion batteries via implantation of amorphous silicon nanolayer in edge-plane activated graphite anodes. *Nature Communications* **2017**, *8* (1), 812.

46. Son, I. H.; Park, J. H.; Park, S.; Park, K.; Han, S.; Shin, J.; Doo, S.-G.; Hwang, Y.; Chang, H.; Choi, J. W., Graphene balls for lithium rechargeable batteries with fast charging and high volumetric energy densities. *Nature Communications* **2017**, *8* (1), 1561.

47. Meyer, C.; Bockholt, H.; Haselrieder, W.; Kwade, A., Characterization of the calendering process for compaction of electrodes for lithium-ion batteries. *Journal of Materials Processing Technology* **2017**, *249*, 172-178.

48. Sharma, R. A.; Seefurth, R. N., Thermodynamic Properties of the Lithium-Silicon System. *J. Electrochem. Soc.* **1976**, *123* (12), 1763-1768.

49. Tagawa, M.; Ema, T.; Kinoshita, H.; Ohmae, N.; Umeno, M.; Minton, T. K., Formation of Thin Oxide Films on Room-Temperature Silicon (100) by Exposure to a Neutral Beam of Hyperthermal Atomic and Molecular Oxygen. *Japanese Journal of Applied Physics* **1998**, *37* (Part 2, No. 12A), L1455-L1457.

50. Ashuri, M.; He, Q.; Shaw, L. L., Silicon as a potential anode material for Li-ion batteries: where size, geometry and structure matter. *Nanoscale* **2016**, *8* (1), 74-103.

51. Obrovac, M. N.; Krause, L. J., Reversible Cycling of Crystalline Silicon Powder. *J. Electrochem. Soc.* **2007**, *154* (2), A103.

52. Chan, C. K.; Peng, H.; Liu, G.; McIlwrath, K.; Zhang, X. F.; Huggins, R. A.; Cui, Y., Highperformance lithium battery anodes using silicon nanowires. *Nature Nanotechnology* **2008**, *3* (1), 31-35.

53. Cho, J.-H.; Picraux, S. T., Silicon Nanowire Degradation and Stabilization during Lithium Cycling by SEI Layer Formation. *Nano Letters* **2014**, *14* (6), 3088-3095.

54. Kitada, K.; Pecher, O.; Magusin, P. C. M. M.; Groh, M. F.; Weatherup, R. S.; Grey, C. P., Unraveling the Reaction Mechanisms of SiO Anodes for Li-Ion Batteries by Combining in Situ 7Li and ex Situ 7Li/29Si Solid-State NMR Spectroscopy. *Journal of the American Chemical Society* **2019**, *141* (17), 7014-7027.

55. Wu, H.; Chan, G.; Choi, J. W.; Ryu, I.; Yao, Y.; McDowell, M. T.; Lee, S. W.; Jackson, A.; Yang, Y.; Hu, L.; Cui, Y., Stable cycling of double-walled silicon nanotube battery anodes through solid–electrolyte interphase control. *Nature Nanotechnology* **2012**, *7* (5), 310-315.

56. Sitinamaluwa, H. S.; Li, H.; Wasalathilake, K. C.; Wolff, A.; Tesfamichael, T.; Zhang, S.; Yan, C., Nanoporous SiOx coated amorphous silicon anode material with robust mechanical behavior for high-performance rechargeable Li-ion batteries. *Nano Materials Science* **2019**, *1* (1), 70-76.

57. Xu, Z.; Yang, J.; Li, H.; Nuli, Y.; Wang, J., Electrolytes for advanced lithium ion batteries using silicon-based anodes. *J. Mater. Chem. A* **2019**, *7* (16), 9432-9446.

58. Manthiram, A., A reflection on lithium-ion battery cathode chemistry. *Nature Communications* **2020**, *11* (1), 1550.

59. Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B., LixCoO2 (0<x<-1): A new cathode material for batteries of high energy density. *Mater. Res. Bull.* **1980**, *15* (6), 783-789.

60. Ozawa, K., Lithium-ion rechargeable batteries with LiCoO2 and carbon electrodes: the LiCoO2/C system. *Solid State Ionics* **1994**, *69* (3), 212-221.

61. Delmas, C.; Fouassier, C.; Hagenmuller, P., Structural classification and properties of the layered oxides. *Physica B+C* **1980**, *99* (1), 81-85.

62. Venkatraman, S.; Shin, Y.; Manthiram, A., Phase Relationships and Structural and Chemical Stabilities of Charged Li[sub 1-x]CoO[sub $2-\delta$] and Li[sub 1-x]Ni[sub 0.85]Co[sub 0.15]O[sub $2-\delta$] Cathodes. *Electrochemical and Solid-State Letters* **2003**, *6* (1), A9.

63. Thackeray, M. A., K. & Kim, J. S. Lithium metal oxide electrodes for lithium cells and batteries. US Patent US6677082. 2000.

64. Yabuuchi, N.; Ohzuku, T., Novel lithium insertion material of LiCo1/3Ni1/3Mn1/3O2 for advanced lithium-ion batteries. *J. Power Sources* **2003**, *119-121*, 171-174.

65. Zheng, J.; Kan, W. H.; Manthiram, A., Role of Mn Content on the Electrochemical Properties of Nickel-Rich Layered LiNi0.8–xCo0.1Mn0.1+xO2 (0.0 ≤ x ≤ 0.08) Cathodes for Lithium-Ion Batteries. *ACS Appl Mater Interfaces* **2015**, *7* (12), 6926-6934.

66. Li, W.; Erickson, E. M.; Manthiram, A., High-nickel layered oxide cathodes for lithiumbased automotive batteries. *Nature Energy* **2020**, *5* (1), 26-34.

67. Chen, C. H.; Liu, J.; Stoll, M. E.; Henriksen, G.; Vissers, D. R.; Amine, K., Aluminumdoped lithium nickel cobalt oxide electrodes for high-power lithium-ion batteries. *J. Power Sources* **2004**, *128* (2), 278-285.

68. Li, W.; Dolocan, A.; Oh, P.; Celio, H.; Park, S.; Cho, J.; Manthiram, A., Dynamic behaviour of interphases and its implication on high-energy-density cathode materials in lithium-ion batteries. *Nature Communications* **2017**, *8* (1), 14589.

69. Li, J.; Manthiram, A., A Comprehensive Analysis of the Interphasial and Structural Evolution over Long-Term Cycling of Ultrahigh-Nickel Cathodes in Lithium-Ion Batteries. *Advanced Energy Materials* **2019**, *9* (45), 1902731.

70. Jiang, M.; Key, B.; Meng, Y. S.; Grey, C. P., Electrochemical and Structural Study of the Layered, "Li-Excess" Lithium-Ion Battery Electrode Material Li[Li1/9Ni1/3Mn5/9]O2. *Chem. Mater.* **2009**, *21* (13), 2733-2745.

71. Muto, S.; Sasano, Y.; Tatsumi, K.; Sasaki, T.; Horibuchi, K.; Takeuchi, Y.; Ukyo, Y., Capacity-Fading Mechanisms of LiNiO[sub 2]-Based Lithium-Ion Batteries. *J. Electrochem. Soc.* **2009**, *156* (5), A371.

72. Jung, R.; Metzger, M.; Maglia, F.; Stinner, C.; Gasteiger, H. A., Chemical versus Electrochemical Electrolyte Oxidation on NMC111, NMC622, NMC811, LNMO, and Conductive Carbon. *The Journal of Physical Chemistry Letters* **2017**, *8* (19), 4820-4825.

73. Rinkel, B. L. D.; Hall, D. S.; Temprano, I.; Grey, C. P., Electrolyte Oxidation Pathways in Lithium-Ion Batteries. *Journal of the American Chemical Society* **2020**, *142* (35), 15058-15074.

74. Wandt, J.; Freiberg, A. T. S.; Ogrodnik, A.; Gasteiger, H. A., Singlet oxygen evolution from layered transition metal oxide cathode materials and its implications for lithium-ion batteries. *Materials Today* **2018**, *21* (8), 825-833.

75. House, R. A.; Maitra, U.; Jin, L.; Lozano, J. G.; Somerville, J. W.; Rees, N. H.; Naylor, A. J.; Duda, L. C.; Massel, F.; Chadwick, A. V.; Ramos, S.; Pickup, D. M.; McNally, D. E.; Lu, X.; Schmitt, T.; Roberts, M. R.; Bruce, P. G., What Triggers Oxygen Loss in Oxygen Redox Cathode Materials? *Chem. Mater.* **2019**, *31* (9), 3293-3300.

76. Sun, Y.-K.; Myung, S.-T.; Kim, M.-H.; Prakash, J.; Amine, K., Synthesis and Characterization of Li[(Ni0.8Co0.1Mn0.1)0.8(Ni0.5Mn0.5)0.2]O2 with the Microscale Core–Shell Structure as the Positive Electrode Material for Lithium Batteries. *Journal of the American Chemical Society* **2005**, *127* (38), 13411-13418.

77. Lim, B.-B.; Yoon, S.-J.; Park, K.-J.; Yoon, C. S.; Kim, S.-J.; Lee, J. J.; Sun, Y.-K., Advanced Concentration Gradient Cathode Material with Two-Slope for High-Energy and Safe Lithium Batteries. *Advanced Functional Materials* **2015**, *25* (29), 4673-4680.

78. Li, T.; Yuan, X.-Z.; Zhang, L.; Song, D.; Shi, K.; Bock, C., Degradation Mechanisms and Mitigation Strategies of Nickel-Rich NMC-Based Lithium-Ion Batteries. *Electrochemical Energy Reviews* **2020**, *3* (1), 43-80.

79. Olivetti, E. A.; Ceder, G.; Gaustad, G. G.; Fu, X., Lithium-Ion Battery Supply Chain Considerations: Analysis of Potential Bottlenecks in Critical Metals. *Joule* **2017**, *1* (2), 229-243. 80. Thackeray, M. M.; Johnson, P. J.; de Picciotto, L. A.; Bruce, P. G.; Goodenough, J. B.,

Electrochemical extraction of lithium from LiMn2O4. *Mater. Res. Bull.* **1984**, *19* (2), 179-187.

81. Thackeray, M. M., Structural Fatigue in Spinel Electrodes in High Voltage (4 V) Li/Li[sub x]Mn[sub 2]O[sub 4] Cells. *Electrochemical and Solid-State Letters* **1999**, *1* (1), 7.

82. Thackeray, M. M., Spinel Electrodes for Lithium Batteries. *Journal of the American Ceramic Society* **1999**, *82* (12), 3347-3354.

83. Blyr, A.; Du Pasquier, A.; Amatucci, G.; Tarascon, J. M., Origin of self-discharge mechanism in LiMn2O4-based Li-ion cells: A chemical and electrochemical approach. *Ionics* **1997**, *3* (5), 321-331.

84. Choi, W.; Manthiram, A., Comparison of Metal Ion Dissolutions from Lithium Ion Battery Cathodes. *J. Electrochem. Soc.* **2006**, *153* (9), A1760.

85. Shkrob, I. A.; Kropf, A. J.; Marin, T. W.; Li, Y.; Poluektov, O. G.; Niklas, J.; Abraham, D. P., Manganese in Graphite Anode and Capacity Fade in Li Ion Batteries. *The Journal of Physical Chemistry C* **2014**, *118* (42), 24335-24348.

86. Rossen, E.; Jones, C. D. W.; Dahn, J. R., Structure and electrochemistry of LixMnyNi1-yO2. *Solid State Ionics* **1992**, *57* (3), 311-318.

87. Armstrong, A. R.; Holzapfel, M.; Novák, P.; Johnson, C. S.; Kang, S.-H.; Thackeray, M. M.; Bruce, P. G., Demonstrating Oxygen Loss and Associated Structural Reorganization in the Lithium Battery Cathode Li[Ni0.2Li0.2Mn0.6]O2. *Journal of the American Chemical Society* **2006**, *128* (26), 8694-8698.

88. Li, W.; Lee, S.; Manthiram, A., High-Nickel NMA: A Cobalt-Free Alternative to NMC and NCA Cathodes for Lithium-Ion Batteries. *Adv. Mater.* **2020**, *32* (33), 2002718.

89. Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B., Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. *J. Electrochem. Soc.* **1997**, *144* (4), 1188-1194.

90. Malik, R.; Abdellahi, A.; Ceder, G., A Critical Review of the Li Insertion Mechanisms in LiFePO4Electrodes. *J. Electrochem. Soc.* **2013**, *160* (5), A3179-A3197.

91. Ravet, N.; Chouinard, Y.; Magnan, J. F.; Besner, S.; Gauthier, M.; Armand, M., Electroactivity of natural and synthetic triphylite. *J. Power Sources* **2001**, *97-98*, 503-507.

92. Kang, B.; Ceder, G., Battery materials for ultrafast charging and discharging. *Nature* **2009**, *458* (7235), 190-193.

93. Wang, J.; Sun, X., Understanding and recent development of carbon coating on LiFePO4 cathode materials for lithium-ion batteries. *Energy & Environmental Science* **2012**, *5* (1), 5163-5185.

94. Lambert, F. Tesla secures approval for new Model 3 with cheaper lithium iron phosphate batteries. <u>https://electrek.co/2020/06/11/tesla-secures-approval-model-3-cheaper-lithium-iron-phosphate-batteries/</u>.

95. Okada, S.; Sawa, S.; Egashira, M.; Yamaki, J.-i.; Tabuchi, M.; Kageyama, H.; Konishi, T.; Yoshino, A., Cathode properties of phospho-olivine LiMPO4 for lithium secondary batteries. *J. Power Sources* **2001**, *97-98*, 430-432.

96. Huang, H.; Yin, S.-C.; Kerr, T.; Taylor, N.; Nazar, L. F., Nanostructured Composites: A High Capacity, Fast Rate Li3V2(PO4)3/Carbon Cathode for Rechargeable Lithium Batteries. *Adv. Mater.* **2002**, *14* (21), 1525-1528.

97. Masquelier, C.; Croguennec, L., Polyanionic (Phosphates, Silicates, Sulfates) Frameworks as Electrode Materials for Rechargeable Li (or Na) Batteries. *Chemical Reviews* **2013**, *113* (8), 6552-6591.

98. Fong, R.; von Sacken, U.; Dahn, J. R., Studies of Lithium Intercalation into Carbons
Using Nonaqueous Electrochemical Cells. *J. Electrochem. Soc.* 1990, *137* (7), 2009-2013.
99. Guyomard, D.; Tarascon, J. M., Rechargeable Li1 + x Mn2 O 4 / Carbon Cells with a New
Electrolyte Composition: Potentiostatic Studies and Application to Practical Cells. *J. Electrochem. Soc.* 1993, *140* (11), 3071-3081.

100. Aurbach, D.; Gamolsky, K.; Markovsky, B.; Gofer, Y.; Schmidt, M.; Heider, U., On the use of vinylene carbonate (VC) as an additive to electrolyte solutions for Li-ion batteries. *Electrochim. Acta* **2002**, *47* (9), 1423-1439.

101. Markevich, E.; Salitra, G.; Aurbach, D., Fluoroethylene Carbonate as an Important Component for the Formation of an Effective Solid Electrolyte Interphase on Anodes and Cathodes for Advanced Li-Ion Batteries. *ACS Energy Lett* **2017**, *2* (6), 1337-1345.

102. Smart, M. C.; Ratnakumar, B. V.; Surampudi, S., Electrolytes for Low-Temperature Lithium Batteries Based on Ternary Mixtures of Aliphatic Carbonates. *J. Electrochem. Soc.* **1999**, *146* (2), 486-492.

103. Herreyre, S.; Huchet, O.; Barusseau, S.; Perton, F.; Bodet, J. M.; Biensan, P., New Liion electrolytes for low temperature applications. *J. Power Sources* 2001, *97-98*, 576-580.
104. Smart, M. C.; Ratnakumar, B. V.; Surampudi, S., Use of Organic Esters as Cosolvents in Electrolytes for Lithium-Ion Batteries with Improved Low Temperature Performance. *J. Electrochem. Soc.* 2002, *149* (4), A361.

105. Smart, M. C.; Ratnakumar, B. V.; Chin, K. B.; Whitcanack, L. D., Lithium-Ion Electrolytes Containing Ester Cosolvents for Improved Low Temperature Performance. *J. Electrochem. Soc.* **2010**, *157* (12), A1361.

106. Smart, M. C.; Lucht, B. L.; Dalavi, S.; Krause, F. C.; Ratnakumar, B. V., The Effect of Additives upon the Performance of MCMB/LiNixCo1–xO2Li-Ion Cells Containing Methyl Butyrate-Based Wide Operating Temperature Range Electrolytes. *J. Electrochem. Soc.* **2012**, *159* (6), A739-A751.

107. Ma, X.; Li, J.; Glazier, S. L.; Ma, L.; Gering, K. L.; Dahn, J. R., A study of highly conductive ester co-solvents in Li[Ni0.5Mn0.3Co0.2]O2/Graphite pouch cells. *Electrochim. Acta* **2018**, *270*, 215-223.

108. Hall, D. S.; Eldesoky, A.; Logan, E. R.; Tonita, E. M.; Ma, X.; Dahn, J. R., Exploring Classes of Co-Solvents for Fast-Charging Lithium-Ion Cells. *J. Electrochem. Soc.* **2018**, *165* (10), A2365-A2373.

109. Li, J.; Li, H.; Ma, X.; Stone, W.; Glazier, S.; Logan, E.; Tonita, E. M.; Gering, K. L.; Dahn, J. R., Methyl Acetate as a Co-Solvent in NMC532/Graphite Cells. *J. Electrochem. Soc.* **2018**, *165* (5), A1027-A1037.

110. Hasa, I.; Haregewoin, A. M.; Zhang, L.; Tsai, W.-Y.; Guo, J.; Veith, G. M.; Ross, P. N.; Kostecki, R., Electrochemical Reactivity and Passivation of Silicon Thin-Film Electrodes in Organic Carbonate Electrolytes. *ACS Appl Mater Interfaces* **2020**, *12* (36), 40879-40890.

111. Yamada, Y.; Yamada, A., Review—Superconcentrated Electrolytes for Lithium Batteries. *J. Electrochem. Soc.* **2015**, *162* (14), A2406-A2423.

112. Yamada, Y.; Wang, J.; Ko, S.; Watanabe, E.; Yamada, A., Advances and issues in developing salt-concentrated battery electrolytes. *Nature Energy* **2019**, *4* (4), 269-280.

113. Yamada, Y.; Takazawa, Y.; Miyazaki, K.; Abe, T., Electrochemical Lithium Intercalation into Graphite in Dimethyl Sulfoxide-Based Electrolytes: Effect of Solvation Structure of Lithium Ion. *The Journal of Physical Chemistry C* **2010**, *114* (26), 11680-11685.

114. Yamada, Y.; Yaegashi, M.; Abe, T.; Yamada, A., A superconcentrated ether electrolyte for fast-charging Li-ion batteries. *Chem Commun* **2013**, *49* (95), 11194-11196.

115. Yamada, Y.; Furukawa, K.; Sodeyama, K.; Kikuchi, K.; Yaegashi, M.; Tateyama, Y.; Yamada, A., Unusual Stability of Acetonitrile-Based Superconcentrated Electrolytes for Fast-Charging Lithium-Ion Batteries. *Journal of the American Chemical Society* **2014**, *136* (13), 5039-5046.

116. Chen, S.; Zheng, J.; Mei, D.; Han, K. S.; Engelhard, M. H.; Zhao, W.; Xu, W.; Liu, J.; Zhang, J.-G., High-Voltage Lithium-Metal Batteries Enabled by Localized High-Concentration Electrolytes. *Adv. Mater.* **2018**, *30* (21), 1706102.

117. Zheng, J.; Lochala, J. A.; Kwok, A.; Deng, Z. D.; Xiao, J., Research Progress towards Understanding the Unique Interfaces between Concentrated Electrolytes and Electrodes for Energy Storage Applications. *Advanced Science* **2017**, *4* (8), 1700032.

118. Cao, X.; Jia, H.; Xu, W.; Zhang, J.-G., Review—Localized High-Concentration Electrolytes for Lithium Batteries. *J. Electrochem. Soc.* **2021**, *168* (1), 010522.

119. Čao, X.; Xu, Y.; Zhang, L.; Engelhard, M. H.; Zhong, L.; Ren, X.; Jia, H.; Liu, B.; Niu, C.; Matthews, B. E.; Wu, H.; Arey, B. W.; Wang, C.; Zhang, J.-G.; Xu, W., Nonflammable Electrolytes for Lithium Ion Batteries Enabled by Ultraconformal Passivation Interphases. *ACS Energy Lett* **2019**, *4* (10), 2529-2534.

120. Chen, S.; Zheng, J.; Yu, L.; Ren, X.; Engelhard, M. H.; Niu, C.; Lee, H.; Xu, W.; Xiao, J.; Liu, J.; Zhang, J.-G., High-Efficiency Lithium Metal Batteries with Fire-Retardant Electrolytes. *Joule* **2018**, *2* (8), 1548-1558.

121. Jia, H.; Zou, L.; Gao, P.; Cao, X.; Zhao, W.; He, Y.; Engelhard, M. H.; Burton, S. D.; Wang, H.; Ren, X.; Li, Q.; Yi, R.; Zhang, X.; Wang, C.; Xu, Z.; Li, X.; Zhang, J.-G.; Xu, W., High-Performance Silicon Anodes Enabled By Nonflammable Localized High-Concentration Electrolytes. *Advanced Energy Materials* **2019**, *9* (31), 1900784.

122. Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K., "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **2015**, *350* (6263), 938.

123. Yang, C.; Chen, J.; Qing, T.; Fan, X.; Sun, W.; von Cresce, A.; Ding, M. S.; Borodin, O.; Vatamanu, J.; Schroeder, M. A.; Eidson, N.; Wang, C.; Xu, K., 4.0 V Aqueous Li-Ion Batteries. *Joule* **2017**, *1* (1), 122-132.

124. Yang, C.; Chen, J.; Ji, X.; Pollard, T. P.; Lü, X.; Sun, C.-J.; Hou, S.; Liu, Q.; Liu, C.; Qing, T.; Wang, Y.; Borodin, O.; Ren, Y.; Xu, K.; Wang, C., Aqueous Li-ion battery enabled by halogen conversion–intercalation chemistry in graphite. *Nature* 2019, *569* (7755), 245-250.
125. Droguet, L.; Grimaud, A.; Fontaine, O.; Tarascon, J.-M., Water-in-Salt Electrolyte (WiSE) for Aqueous Batteries: A Long Way to Practicality. *Advanced Energy Materials* 2020, *10* (43), 2002440.

126. Du, Z.; Wood, D. L.; Daniel, C.; Kalnaus, S.; Li, J., Understanding limiting factors in thick electrode performance as applied to high energy density Li-ion batteries. *Journal of Applied Electrochemistry* **2017**, *47* (3), 405-415.

127. Kuang, Y.; Chen, C.; Kirsch, D.; Hu, L., Thick Electrode Batteries: Principles, Opportunities, and Challenges. *Advanced Energy Materials* **2019**, *9* (33), 1901457.

128. Li, A.; Yuen, A. C.; Wang, W.; De Cachinho Cordeiro, I. M.; Wang, C.; Chen, T. B.; Zhang, J.; Chan, Q. N.; Yeoh, G. H., A Review on Lithium-Ion Battery Separators towards Enhanced Safety Performances and Modelling Approaches. *Molecules* **2021**, *26* (2).

129. Wang, H.; Liu, Y.; Li, Y.; Cui, Y., Lithium Metal Anode Materials Design: Interphase and Host. *Electrochemical Energy Reviews* **2019**, *2* (4), 509-517.

130. Sharafi, A.; Meyer, H. M.; Nanda, J.; Wolfenstine, J.; Sakamoto, J., Characterizing the Li–Li7La3Zr2O12 interface stability and kinetics as a function of temperature and current density. *J. Power Sources* **2016**, *302*, 135-139.

131. Schmidt, R. D.; Sakamoto, J., In-situ, non-destructive acoustic characterization of solid state electrolyte cells. *J. Power Sources* **2016**, *324*, 126-133.

132. Aguesse, F.; Manalastas, W.; Buannic, L.; Lopez del Amo, J. M.; Singh, G.; Llordés, A.; Kilner, J., Investigating the Dendritic Growth during Full Cell Cycling of Garnet Electrolyte in Direct Contact with Li Metal. *ACS Appl Mater Interfaces* **2017**, *9* (4), 3808-3816.

133. Basappa, R. H.; Ito, T.; Yamada, H., Contact between Garnet-Type Solid Electrolyte and Lithium Metal Anode: Influence on Charge Transfer Resistance and Short Circuit Prevention. *J. Electrochem. Soc.* **2017**, *164* (4), A666-A671.

134. Swamy, T.; Park, R.; Sheldon, B. W.; Rettenwander, D.; Porz, L.; Berendts, S.; Uecker, R.; Carter, W. C.; Chiang, Y.-M., Lithium Metal Penetration Induced by Electrodeposition through Solid Electrolytes: Example in Single-Crystal Li6La3ZrTaO12Garnet. *J. Electrochem. Soc.* **2018**, *165* (16), A3648-A3655.

135. Han, F.; Westover, A. S.; Yue, J.; Fan, X.; Wang, F.; Chi, M.; Leonard, D. N.; Dudney, N. J.; Wang, H.; Wang, C., High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes. *Nature Energy* **2019**, *4* (3), 187-196.

136. Kazyak, E.; Garcia-Mendez, R.; LePage, W. S.; Sharafi, A.; Davis, A. L.; Sanchez, A. J.; Chen, K.-H.; Haslam, C.; Sakamoto, J.; Dasgupta, N. P., Li Penetration in Ceramic Solid Electrolytes: Operando Microscopy Analysis of Morphology, Propagation, and Reversibility. *Matter* **2020**, *2* (4), 1025-1048.

137. Pervez, S. A.; Cambaz, M. A.; Thangadurai, V.; Fichtner, M., Interface in Solid-State Lithium Battery: Challenges, Progress, and Outlook. *ACS Appl Mater Interfaces* **2019**, *11* (25), 22029-22050.

138. Chen, R.; Li, Q.; Yu, X.; Chen, L.; Li, H., Approaching Practically Accessible Solid-State Batteries: Stability Issues Related to Solid Electrolytes and Interfaces. *Chemical Reviews* **2020**, *120* (14), 6820-6877.

139. Banerjee, A.; Wang, X.; Fang, C.; Wu, E. A.; Meng, Y. S., Interfaces and Interphases in All-Solid-State Batteries with Inorganic Solid Electrolytes. *Chemical Reviews* **2020**, *120* (14), 6878-6933.

140. Xu, L.; Tang, S.; Cheng, Y.; Wang, K.; Liang, J.; Liu, C.; Cao, Y.-C.; Wei, F.; Mai, L., Interfaces in Solid-State Lithium Batteries. *Joule* **2018**, *2* (10), 1991-2015.

141. Xiao, Y.; Wang, Y.; Bo, S.-H.; Kim, J. C.; Miara, L. J.; Ceder, G., Understanding interface stability in solid-state batteries. *Nature Reviews Materials* **2020**, *5* (2), 105-126.

142. Tong, Z.; Wang, S.-B.; Liao, Y.-K.; Hu, S.-F.; Liu, R.-S., Interface Between Solid-State Electrolytes and Li-Metal Anodes: Issues, Materials, and Processing Routes. *ACS Appl Mater Interfaces* **2020**, *12* (42), 47181-47196.

143. Manthiram, A.; Fu, Y.; Su, Y.-S., Challenges and Prospects of Lithium–Sulfur Batteries. *Accounts of Chemical Research* **2013**, *46* (5), 1125-1134.

144. Liu, T.; Vivek, J. P.; Zhao, E. W.; Lei, J.; Garcia-Araez, N.; Grey, C. P., Current Challenges and Routes Forward for Nonaqueous Lithium–Air Batteries. *Chemical Reviews* **2020**, *120* (14), 6558-6625.

145. Pan, H.; Cheng, Z.; He, P.; Zhou, H., A Review of Solid-State Lithium–Sulfur Battery: Ion Transport and Polysulfide Chemistry. *Energy & Fuels* **2020**, *34* (10), 11942-11961.

146. Kwak, W.-J.; Rosy; Sharon, D.; Xia, C.; Kim, H.; Johnson, L. R.; Bruce, P. G.; Nazar, L. F.; Sun, Y.-K.; Frimer, A. A.; Noked, M.; Freunberger, S. A.; Aurbach, D., Lithium–Oxygen Batteries and Related Systems: Potential, Status, and Future. *Chemical Reviews* **2020**, *120* (14), 6626-6683.

147. Yabuuchi, N.; Kajiyama, M.; Iwatate, J.; Nishikawa, H.; Hitomi, S.; Okuyama, R.; Usui, R.; Yamada, Y.; Komaba, S., P2-type Nax[Fe1/2Mn1/2]O2 made from earth-abundant elements for rechargeable Na batteries. *Nature Materials* **2012**, *11* (6), 512-517.

148. Mariyappan, S.; Wang, Q.; Tarascon, J. M., Will Sodium Layered Oxides Ever Be Competitive for Sodium Ion Battery Applications? *J. Electrochem. Soc.* **2018**, *165* (16), A3714-A3722.

149. Sawicki, M.; Shaw, L. L., Advances and challenges of sodium ion batteries as post lithium ion batteries. *RSC Adv.* **2015**, *5* (65), 53129-53154.

150. Wu, X.; Leonard, D. P.; Ji, X., Emerging Non-Aqueous Potassium-Ion Batteries: Challenges and Opportunities. *Chem. Mater.* **2017**, *29* (12), 5031-5042.

151. Eshetu, G. G.; Elia, G. A.; Armand, M.; Forsyth, M.; Komaba, S.; Rojo, T.; Passerini, S., Electrolytes and Interphases in Sodium-Based Rechargeable Batteries: Recent Advances and Perspectives. *Advanced Energy Materials* **2020**, *10* (20), 2000093.

152. Wang, H.; Zhai, D.; Kang, F., Solid electrolyte interphase (SEI) in potassium ion batteries. *Energy & Environmental Science* **2020**, *13* (12), 4583-4608.

153. Mogensen, R.; Brandell, D.; Younesi, R., Solubility of the Solid Electrolyte Interphase (SEI) in Sodium Ion Batteries. *ACS Energy Lett* **2016**, *1* (6), 1173-1178.

154. Okoshi, M.; Yamada, Y.; Komaba, S.; Yamada, A.; Nakai, H., Theoretical Analysis of Interactions between Potassium Ions and Organic Electrolyte Solvents: A Comparison with Lithium, Sodium, and Magnesium Ions. *J. Electrochem. Soc.* **2016**, *164* (2), A54-A60.

155. Liang, Y.; Dong, H.; Aurbach, D.; Yao, Y., Current status and future directions of multivalent metal-ion batteries. *Nature Energy* **2020**, *5* (9), 646-656.

156. Canepa, P.; Sai Gautam, G.; Hannah, D. C.; Malik, R.; Liu, M.; Gallagher, K. G.; Persson, K. A.; Ceder, G., Odyssey of Multivalent Cathode Materials: Open Questions and Future Challenges. *Chemical Reviews* **2017**, *117* (5), 4287-4341.

157. Matsui, M., Study on electrochemically deposited Mg metal. *J. Power Sources* **2011**, *196* (16), 7048-7055.

158. Shao, Y.; Liu, T.; Li, G.; Gu, M.; Nie, Z.; Engelhard, M.; Xiao, J.; Lv, D.; Wang, C.; Zhang, J.-G.; Liu, J., Coordination Chemistry in magnesium battery electrolytes: how ligands affect their performance. *Scientific Reports* **2013**, *3* (1), 3130.

159. Kitada, A.; Kang, Y.; Uchimoto, Y.; Murase, K., Room-Temperature Electrodeposition of Mg Metal from Amide Salts Dissolved in Glyme-Ionic Liquid Mixture. *J. Electrochem. Soc.* **2013**, *161* (3), D102-D106.

160. Ding, M. S.; Diemant, T.; Behm, R. J.; Passerini, S.; Giffin, G. A., Dendrite Growth in Mg Metal Cells Containing Mg(TFSI)2/Glyme Electrolytes. *J. Electrochem. Soc.* **2018**, *165* (10), A1983-A1990.

161. Davidson, R.; Verma, A.; Santos, D.; Hao, F.; Fincher, C.; Xiang, S.; Van Buskirk, J.; Xie, K.; Pharr, M.; Mukherjee, P. P.; Banerjee, S., Formation of Magnesium Dendrites during Electrodeposition. *ACS Energy Lett* **2019**, *4* (2), 375-376.

162. Davidson, R.; Verma, A.; Santos, D.; Hao, F.; Fincher, C. D.; Zhao, D.; Attari, V.; Schofield, P.; Van Buskirk, J.; Fraticelli-Cartagena, A.; Alivio, T. E. G.; Arroyave, R.; Xie, K.; Pharr, M.; Mukherjee, P. P.; Banerjee, S., Mapping mechanisms and growth regimes of magnesium electrodeposition at high current densities. *Materials Horizons* **2020**, *7* (3), 843-854.

163. Aurbach, D.; Skaletsky, R.; Gofer, Y., The Electrochemical Behavior of Calcium

Electrodes in a Few Organic Electrolytes. J. Electrochem. Soc. 1991, 138 (12), 3536-3545.

164. Ponrouch, A.; Frontera, C.; Bardé, F.; Palacín, M. R., Towards a calcium-based rechargeable battery. *Nature Materials* **2016**, *15* (2), 169-172.

165. Wang, D.; Gao, X.; Chen, Y.; Jin, L.; Kuss, C.; Bruce, P. G., Plating and stripping calcium in an organic electrolyte. *Nature Materials* **2018**, *17* (1), 16-20.

166. Li, Z.; Fuhr, O.; Fichtner, M.; Zhao-Karger, Z., Towards stable and efficient electrolytes for room-temperature rechargeable calcium batteries. *Energy & Environmental Science* **2019**, *12* (12), 3496-3501.

167. Shyamsunder, A.; Blanc, L. E.; Assoud, A.; Nazar, L. F., Reversible Calcium Plating and Stripping at Room Temperature Using a Borate Salt. *ACS Energy Lett* **2019**, *4* (9), 2271-2276.

CHAPTER 2 – UNDERSTANDING THE ELECTRODEPOSITION OF PURE PHASE CRYSTALLINE SnSb FROM DEEP EUTECTIC ETHALINE SOLUTION AND ITS APPLICATION AS A LITHIUM-ION ANODE²

2.1 Overview

The formation of pure phased crystalline SnSb was previously reported through the use of ethaline solution, SnSb being a promising rechargeable battery anode material. An in-depth discussion of the electrodeposition of pure phase SnSb from ethaline is presented in what follows. In this study, understanding the effects of humidity and heating of the deposition solution proved critical to the synthesis. SnSb was also electrochemically cycled in lithium half-cell and its performance was compared with tin rich SnSb, mimicking the impure electrodeposition of SnSb in previous reports.

2.2 Introduction

Energy storage will be of importance for the next decade and beyond given the increased demand for electric vehicles and automakers committed to all-electric vehicles. Secondary batteries have emerged at the forefront of energy-storage materials. Currently, graphite is used as the anode for majority of commercial lithium-ion batteries, although silicon is very slowly beginning to push into commercial uses.¹ Current battery technology can be improved by replacing current graphite anodes. The limitation of graphite is due to its low gravimetric capacity that results from only being able to hold one lithium for every six carbon atoms. Alloy materials have been studied as a potential anode replacement for commercial graphite anodes due to their

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greater volumetric and gravimetric capacities compared to graphite. Alloy anodes have two to ten times the theoretical gravimetric capacity of graphite due to their ability to react with multiple lithium per metal center. One such alloy material, SnSb, has been heavily researched and is a promising material to potentially replace graphite.

Electrodeposition is a scalable process utilized to synthesize materials in a wide variety of applications including energy storage, batteries and capacitors, energy production, photoelectrochemistry and thermoelectric, and through the production of coatings for corrosion resistance.²⁻⁶ Electrodeposition is specifically of interest for battery application as it allows for growth outside of planar substrates, enabling the growth of high surface area, 3D-architecture electrodes. Although electrodeposition was the first reported synthesis for the creation of a Sn-Sb alloy to test in secondary batteries, the synthesis of phased-pure SnSb through electrodeposition was not reported until our recent paper. ^{7, 8} Prior electrodeposition reports resulted in tin rich products with crystalline tin impurities.^{7, 9-13} Instead of an aqueous solution that previous groups have used to synthesized SnSb, our synthesis of SnSb uses ethaline (1:2 molar ratio of choline chloride to ethylene glycol), a deep eutectic solvent of interest due to the suitable electrochemical window for our synthesis, the cheap and easily obtainable materials of choline chloride and ethylene glycol that make up this solvent, and also the biodegradability of the solvent.¹⁴ This solvent also allows direct and single-step electrodeposition of the targeted species with minimal side reactions.

In this study, we describe in depth the electrodeposition process of SnSb and show how careful understanding of the solution is critical to the production of phase-pure SnSb. Although we do have a degree of control of the product, many challenges arise that are dependent on the preparation and use of the solution. The presence of humidity, over time, and the positives and negatives of heating the electrodeposition solution are discussed. The material's performance in a lithium-ion battery will also be evaluated. A common impurity found through electrodeposition

of SnSb, namely excess Sn, was deliberately introduced into the synthesis process. The electrochemical performance of electrodes containing different amounts of excess Sn, thereby mimicking the production of impure Sn-rich SnSb, were compared to phase-pure SnSb, demonstrating the importance of synthesizing the phase-pure material.

2.3 Experimental Methods

2.3.1 Electrodeposition of tin and antimony from ethaline

Baths used for the electrodeposition of Sn and Sb consisted of 50 mM SbCl₃ (Sigma Aldrich, ACS reagent) and 50 mM SnCl₂·2H₂O (Sigma Aldrich, ACS reagent) dissolved in ethaline. Ethaline, the solvent for the electrodepositions, was prepared using 1:2 molar ratio of choline chloride (both Aldrich, purity >98% and VWR, high purity were used) and ethylene glycol (Fisher Scientific), respectively. Choline chloride was heated at reflux in absolute ethanol (Pharmaco, 200 Proof) on a hotplate and recrystallized prior to use. The crystals were then filtered and dried in a vacuum oven at 100°C. The amount of water in choline chloride can greatly dictate the chemistry as discussed later. The solution containing 50 mM SbCl₃ and 50 mM SnCl₂·2H₂O in ethaline was typically heated at 70° C until the solution became homogenous and clear. Electrodeposition was conducted from the baths in a three electrode setup using Chi 660C Potentiostat (CH Instrument) with a platinum mesh counter electrode (100 mesh, Alfa Aesar), silver wire reference electrode, and copper or nickel foil as the working electrode. All copper foils were electrochemically polished in phosphoric acid (H₃PO₄) at a constant potential of 3 V for 30 seconds to remove the oxide layer present on the surface. Nickel foil was cleaned in 0.1 M nitric acid for 30 seconds prior to deposition. Kapton[©] tape was placed on the back of the different foils to allow for deposition to only occur on one side of the film with a controlled surface area. Single step electrodepositions were performed at 25° C with a constant potential of -0.7 V vs Ag/Ag+. Electrochemical studies were performed using electrodepositions performed for 60 seconds.

2.3.2 Characterization

Cyclic voltammetry (CV) was conducted using a three electrode setup, where the working electrode was platinum (BASi, 1.6 mm diameter), the counter electrode was a platinum mesh (100 mesh, Alfa Aesar), and the reference electrode was a silver wire. CVs were conducted within the range of -1.2 V to 1.2 V vs Ag/Ag⁺ at varying scan rates. The solution was studied using direct analysis real time mass spectrometry (DART-MS; Bruker MaXis QTOF with IonSense DART-SVP and Agilent TOF LCMS with Ion Sense DART-100 were used). DART-MS was prepared in negative ion mode and spectra were calibrated using Fomblin Y as standard. The surface of the electrode was studied by scanning electron microscopy (SEM; JOEL JSM-6500F operating at 15 kV). Complementary to this technique, energy-dispersive X-ray spectroscopy (EDS) was used to obtain spectra and analyzed using Aztec software (Oxford Instrument) to calculate the composition and identify the atomic makeup of the electrodeposited films. The crystalline structures present on the electrodeposited electrodes were identified using conventional X-ray diffraction (XRD;Bruker D8 Discover DaVinci, Cu Kα radiation, λ = 1.54184 Å) and glancing angle X-ray diffraction (GAXRD;Bruker D8 Discover Series 1, Cu Kα radiation, λ = 1.54184 Å).

Electrochemical cycling of the electrodeposited electrodes was conducted in Swagelok half-cells. The half-cells were composed of the electrodeposited electrode and lithium metal on opposing ends, with polypropylene separator (MTI Corp) and glass filter (Whatman, Grade GF/A, 21mm) filled with 1.0 M LiPF₆ in dimethyl carbonate (DMC;Sigma Aldrich, battery grade) + 5% by volume vinylene carbonate (Sigma Aldrich). Half-cells were tested through galvanostatic cycling on an Arbin battery tester (BT-2000). The C-rate at which the electrodes were cycled was determined from the theoretical capacity of active material on each electrode. *Ex situ* studies of the electrodes were performed after galvanostatically cycling to the desired state of charge or discharge. The half-cells were then disassembled in an Argon glovebox (<1 ppm O_2) and electrodes were cleaned with DMC prior to studies on the SEM and XRD.

2.4 Discussion and Results

2.4.1 Cyclic voltammogram and electrodeposition of tin and antimony in ethaline

Cyclic voltammetry of the 50 mM SbCl₃ and 50mM SnCl₂·2H₂O in ethaline solution at different scan rates are present in figure 2.1a. Cyclic voltammetry of solely SbCl₃ or SnCl₂·2H₂O in ethaline have been analyzed in our previous paper to help better understand the single-step electrodeposition of SnSb.⁸ The cyclic voltammogram of the solution used for the electrodeposition of phase-pure 1:1 ratio Sn:Sb at a scan rate of 50 mV·s⁻¹ shows two primary reduction peaks corresponding to the reduction of Sb³⁺/Sb⁰ at -0.3 V and Sn²⁺/Sn⁰ occurring at a more negative potential of -0.55 V vs Ag/Ag⁺. During the reverse anodic sweep across the same range, the oxidation of Sn⁰/Sn²⁺ was first seen at -0.3 V followed by the expected Sb⁰/Sb³⁺ process at 0.1 V vs Ag/Ag⁺. Due to the more negative Sn²⁺/Sn⁰ reduction, attempts for co-deposition were performed at more negative potentials than -0.45 V. However, due to the fact that stripping of Sn²⁺ occurs at more positive potentials than -0.45 V vs Ag/Ag⁺, the deposition potential was selected to occur at potentials more negative than -0.45 V to avoid any tin stripping. Due to inconsistent deposition at more positive potentials, -0.7 V was used which resulted in more crystalline electrodeposited products (Figure S2.1). SEM images of depositions at -0.6 V verified the presence of an amorphous deposition product with the presence of polycrystalline amorphous particles on the surface of the electrode. The electrodeposition at -0.7 V resulted in more faceted particles suggesting the formation of SnSb particles and supported by XRD.

The CV of 50 mM SbCl₃ and 50mM SnCl₂·2H₂O in ethaline solution at different scan rates (figure 2.1a) helps understand the deposition conditions and whether co-deposition will occur. Based on data extracted from the variable scan rate CV's, the maximum peak current for the reduction, at ~-0.55 V vs Ag/Ag⁺, is increasing proportionally to the square root of the scan rate (v^{1/2}) (figure 2.1b). This suggests the deposition potential is diffusion controlled and follows Cottrell's law with no other side reactions. The varying scan rates also show an increase in

overpotential when compared to its complementary oxidation peak, with higher scan rates (figure 2.1c), signifying the occurrence of an irreversible deposition occurring at this peak potential. Additionally, with increasing scan rate the ratio of the oxidation peak current at around -0.3 V vs Ag/Ag⁺ (due to Sn⁰/Sn²⁺ oxidation) to the reduction peak current at -0.55 V vs Ag/Ag⁺ decreases. This decrease suggests a degree of irreversible reaction as seen with the change in scan rate (figure 2.1d). This irreversibility is consistent with the co-deposition of both Sn²⁺/Sn⁰ and Sb³⁺/Sb⁰ at -0.55 V vs Ag/Ag⁺, as opposed to the stripping of only Sn²⁺/Sn⁰ at -0.3 V vs Ag/Ag⁺ (figure 2.1a).



Figure 2.1: Cyclic voltammogram of 50 mM SnCl₂·2H₂O and 50 mM SbCl₃ in ethaline at varying scan rates. Data were extrapolated from the varying rate CV's including (a) potential difference between the cathodic peak and anodic peak with respect to scan rate, (b) the current of the cathodic peak with respect to the square root of the scan rate, and (c) the ratio of the anodic peak current to the cathodic peak current versus scan rate. The cathodic peak used is the peak at -0.55 V vs Ag/Ag⁺; the anodic peak used is the peak at -0.3 V vs Ag/Ag⁺.

In order to verify the co-deposition occurring at -0.7 V vs Ag/Ag⁺, the rate of deposition was measured based on length of deposition in each individual Sn and Sb solutions as well as in

a solution containing both the Sn and Sb salts (figure 2.2). The individual Sn and Sb solutions resulted in similar rates of deposition over time. Depositions conducted from the ethaline solution containing both Sn and Sb resulted in a higher overall charge for deposition. When comparing the sum of the individual Sn and Sb depositions at this deposition potential to the deposition from a solution containing both Sn and Sb, the sum of the individual solutions resulted in a lower overall deposition process. This higher magnitude of deposition over time from the solution containing both Sn and Sb suggests a different speciation in the combined Sn and Sb solution during deposition.



Figure 2.2: Coulombs passed (left) and calculated density of product (right) based on the electrodepositions performed at -0.7 V vs Ag/Ag^+ from 50 mM $SnCl_2 \cdot 2H_2O$ and 50 mM $SbCl_3$ in ethaline with varying deposition times.

2.4.2 Effect of water on electrodeposition products

The synthesis of phase-pure SnSb (i.e., with a 1:1 ratio Sn:Sb) through electrodeposition is a simple and direct process. However, different conditions were found to have an effect on the product obtained. Through our synthesis of phase-pure SnSb from an ethaline solution, we observed the presence of water appears to affect the chemistry as both choline chloride and ethylene glycol precursors are hygroscopic. Presented in figure 2.3 are the x-ray diffraction patterns of electrodeposited SnSb products onto copper foil. As shown with the electrodeposited product resulting from the as-prepared solution, which contained Sb and Sn chloride dissolved in the ethaline solution produced using the as-obtained choline chloride and ethylene glycol mixture, crystalline SnSb is made with a minor crystalline phase of Sn present. Heating the ethaline solution at 110°C prior to use, driving off water that is present, resulted in the room temperature electrodeposition of pure crystalline SnSb.

In order to support the hypothesis that the Sn phase is caused by water collected by pristine, but hygroscopic, ethaline, water was introduced back into the previously heated solution, resulting in the re-emergence of the minor, crystalline Sn phase. However, minimal humidity may be acceptable, as the chemistry in ethaline solvent does not change immediately when exposed to ambient room humidity and other conditions. Additional control experiments were conducted to support the hypothesis that heating of the solution is related to the removal of water and not due to changes to the reaction components directly due to heating (Figure S2.2).



Figure 2.3: XRD patterns of -0.7 V vs Ag/Ag⁺ 300 second depositions from 50 mM SnCl₂·2H₂O and 50 mM SbCl₃ in ethaline solution as prepared, heated at 110° C, and after water was introduced into the solution.

In order to verify the possibility that water may play a role in the change of the solution's chemistry and the resulting products, additional experiments were performed where the tin and antimony salts were dissolved into an aqueous solution. These studies were conducted at the same temperature, electrodeposition potential, and time as the ethaline electrodeposition. Figure 2.4 presents the cyclic voltammograms of an aqueous solution containing both Sn and Sb salts at varying pH. XRD patterns from electrodeposition at -0.7 V onto a nickel substrate under the varied pH values examined were also collected. Tuning the aqueous solution to different pH values for deposition is necessary, as it is difficult to determine the exact amount of water and the pH of the nonaqueous ethaline solution. At most pH values between 2.5 to 8, SnSb is the major phase formed from the electrodeposition process as judge by XRD of the electrodeposited product. However, the formation of crystalline tin also occurs in conjunction with the formation of SnSb. At pH 8, the trend is broken and an amorphous hump is formed, which may be due to the formation of amorphous Sn-O and Sb-O products at this basic pH. This presence of tin impurity in aqueous solution helps supplement the suggestion that water collected by the hygroscopic ethaline solution aiding the deposition of crystalline tin during the electrodeposition of SnSb.



Figure 2.4: Cyclic voltammetry (left) and its corresponding XRD patterns (right) from electrodeposition performed at -0.7 V vs Ag/Ag⁺ at varying pH of a 50 mM SnCl₂·2H₂O and 50 mM SbCl₃ aqueous solution.

2.4.3 Excess heating of solution and negative consequences on the synthesis of SnSb

While unwanted moisture in the solution can be reduced by heating the ethaline solution to 110°C, excessive heating extended periods of time has a negative impact on the electrodeposited product. As shown from the cyclic voltammogram of both Sn and Sb salts in ethaline taken after heating the solution at 100°C for different times (figure 2.5a), the reduction and oxidation peaks related to Sn²⁺/Sn⁰ at -0.55 V and -0.3 V vs Ag/Ag⁺, respectively, weaken and disappear with longer heating times. X-ray diffraction reveals the electrodeposition product at -0.7 V onto a nickel substrate using a solution heated for 3 days at 110°C resulted in an amorphous product with a antimony-rich Sn:Sb composition based on EDS. EDS reveals that longer heating at 110°C resulted in a drop in atomic ratio of the deposition from 1 to 1 Sb:Sn ratio

to a 2.5:1 Sb:Sn ratio after 3 days. Further heating the solution for 4 days decreased the tin content in the deposition to 4.5:1 Sb:Sn. At this state, the solution quickly forms a solid gel once it is cooled to room temperature. Interestingly, quick re-heating to reform temporarily the homogenous solution for the solution (starting with a solution that had been heated at 110° C for 4 days) resulted in a slightly higher Sb:Sn of 2.5:1 of the electrodeposited product (i.e., compared to the 4.5:1 Sb:Sn ratio when the solgel crashes out). However, the quick re-heating does not reincorporate all Sn salts back into the solution. Figure 2.5b and c also presents the cyclic voltammograms of individual tin and antimony salt solutions after different times of heating at 110° C. Heating of individual solutions suggests tin is the dominant species affected by heating as judged by cyclic voltammogram of Sn in ethaline (figure 2.5c) where a decrease in cathodic current at -0.5 V, and anodic current at 0.3 V vs Ag/Ag⁺ with longer heating time at 110° C. Meanwhile, heating of the individual antimony in ethaline solution (figure 2.5b) resulted in negligible change in peak currents of the reduction and oxidation of antimony at -0.3 V and 0.2 V vs Ag/Ag⁺, respectively.



Figure 2.5: Cyclic voltammogram of (a) 50 mM SnCl₂·2H₂O and 50 mM SbCl₃ in ethaline, (b) 50 mM SbCl₃ in ethaline, and (c) 50 mM SnCl₂·2H₂O in ethaline solution after different stages of heating at 110° C.

In order to determine why the cyclic voltammetry detects less tin in the solution after longer heating times, analysis of the makeup of the solution was conducted. Using DART-M.S., the solution containing both Sn and Sb in ethaline was studied at the different stages of heating at 110°C to observe any mass to charge changes in the solution (figure 2.6). Comparing the mass spectra (MS) from different heating time lengths to the MS from pristine ethaline, the majority of peaks below 200 m/z, in the solutions containing both the Sn and Sb salts, match the different m/z peaks found in the pristine ethaline solution. For the peaks greater than 200 m/z that are present, a small triplet peak occurring at around 250-260 m/z appears after heating and increases in intensity with longer heating. We theorize that the peaks present in this range may be related to some type of SnCl₂ ethylene glycol complex, as the m/z peaks matches with the predicted mass of SnCl₂ ethylene glycol. The triplet peak present also supports the theory that SnCl₂ may be one of the species present as two chlorines and the two common isotopes found for chlorine are responsible for the triplet. Based on previous the literature on the formation of SnO₂, ethylene glycol heated with different tin salt precursors has been used to form sol-gels.^{15,} ¹⁶ It can be hypothesized that SnCl₂ may be selectively isolated and segregated out of the solution when such sol-gel species are formed. Additional support to this hypothesis is found macroscopically with the visual formation of crystalline-like materials within the solution after long heating times. Extraction of the crystal results in the removal of material in a gel-like consistency (figure S2.3). DART-MS of this gel resulted in peaks at 250-260 m/z range that are identical to the triplet peaks SnCl₂·ethylene glycol.

While we are able to identify the formation of a SnCl₂ ethylene glycol solgel, we are unable to identify the exact chemical bonding within this gel. Previous literature claims the eventual formation of a polyethylene glycol-tin complex with heating, but our mass spectrum suggests only one ethylene glycol is part of the SnCl₂ ethylene glycol complex, and at least the one able to be desorbed and reach the MS detector.¹⁵



Figure 2.6: DART-MS of ethaline and 50 mM $SnCl_2 \cdot 2H_2O$ and 50 mM $SbCl_3$ in ethaline at different states of heating. The sol gel extracted from heating the 50 mM $SnCl_2 \cdot 2H_2O$ and 50 mM $SbCl_3$ in ethaline solution at 110° C is presented at the bottom. The blue region represents the peaks below 200 m/z matching with ethaline. The purple region identifies the presence of a triple peak growing over time.

Electrical conductivity measurements were also conducted versus heating time in ambient environment to study the change in ionic contents in the solution (figure S2.4). As expected, with increasing temperature, the conductivity of the solutions increases due to higher rates of diffusion. With solutions that were left out at ambient temperature, the observed conductivity (i.e., of conducting ions) also increases, suggesting a possible change in speciation and also the probable increase in water in the solution over time. Supporting this, the addition of water into the solution leads to higher conductivity compared to either the as-prepared solutions or minimally heated solutions. These conductivity measurements adds to the hypothesis that over time, humidity changes the speciation of the solution over time. Excessively heating the solution at 110° C for 3 days or greater decreases the conductivity of the solution and supports previous observation of decreased ion activity in the solution due to the formation of solgel. Overall, careful control of the speciation present in the solution is crucial to formation of the desired phased-pure SnSb and resisting undesired Sn and Sb- rich electrodeposited products.

2.4.4 Electrochemical performance of pure SnSb as a Lithium-ion anode

Electrochemical tests were conducted in half cells versus lithium to understand the material's capacity, rate capability, and stability compared to other Sn, Sb or impure Sn-Sb electrodeposited films. SnSb electrodeposited onto Ni foil was used as electrodes for these electrochemical tests, as opposed to the use of copper substrates, due to a previous study by our group showing detrimental migration of copper into electrochemically active antimonide electrodes.¹⁷ To study the cyclability of our electrodeposited SnSb, the half cells were cycled at a C/2 rate between 0.01 V – 1.5 V vs Li/Li⁺ as presented in figure 2.7. Electrodeposited Sn and Sb through ethaline solution at similar conditions were also electrochemically tested to compare to the as synthesized SnSb. Over the 1000 cycles presented, SnSb was higher in overall capacity than either of the Sb and Sn samples. SnSb combined the stability of Sb for long cycling with the higher theoretical capacity of Sn. SnSb does have an initial irreversible capacity loss of 35% when comparing the second cycle with the first cycle, a loss that is widely believe to be due to the initial formation of a solid electrolyte interface (SEI). The capacity retained is greater than 97% in subsequent cycles. When comparing with the second cycle, with a gravimetric capacity of 757 mAh/g, the SnSb undergoes 400 cycles (603 mAh/g at cycle 401) before it has lost 20% of its initial capacity.

Rate capability tests of SnSb electrodes were performed to identify the capacities at which the SnSb can operate at different charge densities. Electrodeposited SnSb was able to cycle versus lithium with specific gravimetric capacities of 693 mAh/g at C/2 rate, 690 mAh/g at 1C rate, 675 mAh/g at 2C rate, 660 mAh/g at 5C rate, 630 mAh/g at 10C rate, and 600 mAh/g at 20C rate.

Returning to C/2 rate from the higher cycling rates at the end showed full capacity recovery and stability of the material towards cycling at the higher rates.



Figure 2.7: Galvanostatic cycling of electrodeposited SnSb, Sn, and Sb (left) between the range of 0.01 V – 1.5 V at C/2 rate. Rate capability of electrodeposited SnSb in a lithium half-cell at different current rates.

Differential capacity graphs were derived from the galvanostatic cycling data; the differential capacity graphs are important to review the electrochemical lithiation and delithiation phases that the electrodeposited SnSb goes through. Presented in figure 2.8 are the differential capacity graphs of electrodeposited SnSb, Sn, and Sb. The reactions between Sb and lithium, which previous reports say results in Li₃Sb, occurs between 0.8 V and 1.1 V vs Li/Li⁺ as highlighted in red.¹⁸⁻²⁰ Reactions between Sn and lithium, forming Li_{4.4}Sn, is presented in blue and appears between 0.4 V and 0.8 V vs Li/Li⁺. The lithiation and delithiation of SnSb involves the lithiation and delithiation events of both the individual Sn and Sb. Overall, cycling of SnSb results in the broadening of the electrochemical features in later cycles, postulated to be due to to the growing resistance from uneven formation of SEI on the electrode surface.



Figure 2.8: Differential capacity plots (dQ/dV) of electrodeposited (a) Sb (b) SnSb and (c) Sn during their first two cycles. Differential capacity plot of (d) SnSb galvanostatically cycled at C/2 rate after its 1st, 2nd, 5th, 10th, 50th, 100th, and 150th cycles.

Surface morphology during cycling, visualized through ex-situ SEM images, shows the expected strain from multiple lithiation and delithiation events (figure 2.9). The surface of the pristine sample showed particles of 150 nm size. After the first lithiation and delithiation cycle, the SEM images reveal resulting smaller particle size of <100 nm. After 10 cycles, the surface of the electrode begins to reveal <100 nm width fractures. After 50 cycles, the surface presents more fractures present on the electrode. However, a different morphology is seen to form on the surface of the electrode that is less crystalline, suggesting formation of a strongly adhering SEI on the surface of the electrode.

Ex-situ XRD was performed concurrently with the ex-situ SEM to study the changes in crystallinity over cycling (figure 2.9). After the first lithiation and delithiation, crystalline SnSb is seen to be present, verifying the reformation of SnSb after delithiation of the electrode material, as seen in previous SnSb studies.^{19, 21, 22} Further cycling of the electrode shows the reformation

still occurs up to cycle 50, but crystallinity decreases drastically. This loss of crystallinity is believed to be due to the loss of long range ordering of the crystalline material and formation of smaller crystallite sizes with cycling.



Figure 2.9: *Ex situ* studies were performed on electrodeposited SnSb galvanostatically cycled at C/2 rate stopped at different points of cycling. SEM images of the changes that occur on the surface of the electrode (top) during specific stages of cycling and their corresponding XRD patterns (bottom) were collected.

2.4.5 Detrimental effects of impure synthesis on lithium-ion lifetime

In order to compare the performance of pure SnSb produced in this work to the impure production seen in previous reports, a controlled way of forming tin rich SnSb was necessary. Using the same ethaline solvent, the impure and tin rich SnSb samples were intentionally synthesized containing concentrations equal to the targeted Sn:Sb ratios. Increasing the Sn content past the 1:1 Sn:Sb ratio results in the production of crystalline tin, as shown by XRD (figure 2.10a). Also presented through the XRD patterns is the continuous increase in intensity of

crystalline tin as deposition from higher concentration of tin solution is performed. Using the SEM-EDS, the composition of the electrode created was verified to be in similar ratio as the initial solution concentration. The introduction of excess tin into the system can be monitored using differential capacity plots within the range at which tin and antimony lithiate (figure 2.10b). As stated in the previous section, the lithiation and delithiation of SnSb combines the different phases that single phased Sn and Sb electrodes undergoes. As we increase the Sn content to artificially mimic the production of impure, Sn-rich SnSb, an increase in activity related to Sn lithiation and delithiation is present as judge by the differential capacity plot (figure 2.10b). Conversely, due to the decrease of Sb content in the overall cell, dQ/dV is visibly decreased related to the Sb lithiation and delithiation. The purity of our SnSb and successful introduction of tin into the system is also supported in the differential capacity plots shown in our previous study of SnSb as a Na-ion anode.⁸

Testing of the tin rich SnSb electrodes is important as it tests the importance of the purity of SnSb on the stability of the system. Figure 2.10c presents the galvanostatic cycling of the different ratio of Sn:SnSb electrodeposited electrodes between 0.01 V and 1.5 V vs Li/Li⁺ at C/2 rate. Artificially made impure, Sn-rich SnSb samples resulted in a decreased capacity within the first 200 cycles (>10% capacity lost within 200 cycles based on figure 2.10c). Pure tin had the highest initial capacity loss with 94% loss after 200 cycles, while SnSb had the lowest initial capacity loss with 7% after 200 cycles. Of the tin-rich SnSb electrodes, 1:3 Sn:SnSb had 13% capacity loss, 1:1 Sn:SnSb had 19% capacity loss, and 3:1 Sn:SnSb had loss 26% of its capacity in 200 cycles. This significant initial drop may be due to the large volumentric expansion and instability of the crystalline Sn regions present in the film. Eventually, the capacity decrease slows down in later cycles (>200) for tin rich SnSb electrodes may be related to the SnSb regions left behind. The slow decrease in capacity during this state of cycling may be related to the slow

growth of SEI on newly exposed surface. Figure 2.10d summarizes at what point each electrode falls below 80% capacity retention, with respect to the capacity at the second cycle. With increasing Sn impurity present, the Sn-Sb electrode begins to fall below this benchmark at earlier cycles. Reformation of SnSb in lithium system has been shown in previous literature and hinted to some benefits related to this reformation.^{19, 21, 22} While the phases during insertion are different, recent studies on the reformation of SnSb tested against sodium supports synergistic effects of SnSb reformation on the cycle life of the material.^{8, 23} The reformation of SnSb may have some synergistic effect in mitigating overall stress and expansion during lithiation/delithiation that pure Sn does not possess.



Figure 2.10: Depositions with varying amounts of Sn:SnSb were prepared and characterized using a) XRD patterns. The electrochemical testing of the depositions were preformed showing b) the differential capacity (dQ/dV) plots and c) the galvanostatic cycling data between the potential window of 0.01 V – 1.5 V in a lithium half-cell. The galvanostatic cycling data is summarized (d) in a graph which shows when the electrodes fall below 80% capacity retained, based on the second cycle.

2.5 Conclusion

In summary, the synthesis of pure SnSb through electrodeposition was carefully developed and key synthesis parameters relating to the presence of water and heating the solution were identified. Synthesis in ethaline solution was found to be highly selective, although this hydroscopic medium can show impurity over time in humid atmospheres. Heating to 110° C removes excess water sufficient to allow phased-pure SnSb to be prepared. However, excessive heating at 110° C was found to have a negative effect. Specifically, heating at 110° C for 3 days led to the formation of a sol-gel with the resulting electrodeposition product from this solution being antimony-rich SnSb. Electrodeposited SnSb was studied as a Li-ion battery, showing stability and falling below 80% capacity only after 400 cycles. In order to study the necessity of a phased-pure electrodeposition process, samples were prepared containing tin-rich products to mimic the impure tin-rich SnSb production. Electrochemical data show the negative effect on the electrode's cyclability as Sn content increases and the importance of purity on the lifetime of SnSb anodes. Despite Sn ideally supplying higher energy density to the overall battery, the stress from the lithiation of impure regions of Sn in our electrodeposition is detrimental to the battery's overall performance and lifetime. Intrinsically, SnSb is found to help access the higher capacity Sn possess, while minimizing the stress and expansion related to this process. Extrinsic of the material's properties, engineering the electrode material through additives, mechanical network, and coatings promises to help access higher Sn content electrodes.
2.6 References

1. A. Scott, In the battery materials world, the anode's time has come., in *Chemical & Engineering News*, American Chemical Society (2019).

2. A. Lahiri and F. Endres, *J. Electrochem. Soc.*, **164**, D597 (2017).

3. A. González, E. Goikolea, J. A. Barrena and R. Mysyk, *Renewable and Sustainable Energy Reviews*, **58**, 1189 (2016).

4. G. V. Govindaraju, G. P. Wheeler, D. Lee and K.-S. Choi, *Chem. Mater.*, **29**, 355 (2017).

5. F. Xiao, C. Hangarter, B. Yoo, Y. Rheem, K.-H. Lee and N. V. Myung, *Electrochim. Acta*, **53**, 8103 (2008).

6. G. E. F. Brewer, C. American Chemical Society. Division of Organic and C. Plastics, *Electrodeposition of coatings : a symposium sponsored by the Division of Organic Coatings and Plastics Chemistry at the 161st meeting of the American Chemical Society, Los Angeles, Calif., March 31-April 1, 1971*, Washington, D.C. : American Chemical Society, Washington, D.C. (1973).

7. J. Yang, M. Winter and J. O. Besenhard, *Solid State Ionics*, **90**, 281 (1996).

8. J. Ma and A. L. Prieto, *Chem Commun* (2019).

9. J. O. Besenhard, J. Yang and M. Winter, J. Power Sources, 68, 87 (1997).

10. H. P. Zhao, C. Y. Jiang, X. M. He and J. G. Ren, *J. Power Sources*, **184**, 532 (2008).

11. H. P. Zhao, G. Zhang, C. Y. Jiang and X. M. He, *lonics*, **18**, 11 (2012).

12. Q. L. Jiang, D. Z. Hu, M. Q. Jia and R. S. Xue, *Applied Surface Science*, **321**, 109 (2014).

13. S. Sengupta, A. Patra, M. Akhtar, K. Das, S. B. Majumder and S. Das, *J Alloys Compd.*, **705**, 290 (2017).

14. A. P. Abbott, R. C. Harris, F. Holyoak, G. Frisch, J. Hartley and G. R. T. Jenkin, *Green Chemistry*, **17**, 2172 (2015).

15. G. Zhang and M. Liu, *Journal of Materials Science*, **34**, 3213 (1999).

16. A. Debataraja, D. W. Zulhendri, B. Yuliarto, Nugraha, Hiskia and B. Sunendar, *Procedia Engineering*, **170**, 60 (2017).

17. M. C. Schulze, R. K. Schulze and Amy L. Prieto, J. Mater. Chem. A, 6, 12708 (2018).

18. L. Aldon, A. Garcia, J. Olivier-Fourcade, J.-C. Jumas, F. J. Fernández-Madrigal, P.

Lavela, C. P. Vicente and J. L. Tirado, *J. Power Sources*, **119-121**, 585 (2003).

19. F. J. Fernandez-Madrigal, P. Lavela, C. P. Vicente and J. L. Tirado, *Chem. Mater.*, **14**, 2962 (2002).

20. P. Antitomaso, B. Fraisse, L. Stievano, S. Biscaglia, D. Ayme-Perrot, P. Girard, M. T. Sougrati and L. Monconduit, *J. Mater. Chem. A*, **5**, 6546 (2017).

21. C. M. Park and H. J. Sohn, *Electrochim. Acta*, **54**, 6367 (2009).

22. S. C. Chao, Y. F. Song, C. C. Wang, H. S. Sheu, H. C. Wu and N. L. Wu, *J. Phys. Chem. C*, **115**, 22040 (2011).

23. W. P. Kalisvaart, H. Xie, B. C. Olsen, E. J. Luber and J. M. Buriak, *ACS Applied Energy Materials*, **2**, 5133 (2019).

CHAPTER 3 – ELECTRODEPOSITION OF PURE PHASE SnSb EXHIBITING HIGH STABILITY AS A SODIUM-ION BATTERY ANODE³

3.1 Overview

Electrodeposition of pure phase SnSb is reported for the first time. The purity of the product is important, as the impure phase is found to be detrimental to the material's lifetime as a sodium-ion anode. The directly deposited electrode was able to retain 95% capacity after 300 cycles, and only fall below 80% capacity retention after 800 cycles when cycled versus sodium.

3.2 Introduction

Secondary batteries play a major role in energy storage as we slowly transition from nonrenewable sources, such as fossil fuels, to cleaner and more sustainable storage methods. Of the secondary battery technologies, lithium-ion batteries are currently utilized in applications ranging from portable devices to all-electric vehicles. In recent years there has been an influx in the research on sodium-ion batteries as a substitute for lithium-ion in certain technologies, such as large grid storage, due to sodium's higher abundance and low cost. The traditional anode material for lithium-ion batteries, graphite, does not perform well as a sodium-ion anode.^{1,2} This is due to the larger size of Na⁺ ions when compared to Li⁺ ions, which makes graphite not a compatible host. This motivates the need for optimal Na-ion anodes that can exhibit high capacity and long cycle life. Currently, most investigations on sodium anode materials revolve around hard carbon.³ However, hard carbon exhibits poor cycling performance and can result in the plating and dendritic growth of sodium metal on the surface, which is a safety hazard.

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The motivation in studying alloy anode materials is their greater volumetric and gravimetric capacities when compared to hard carbon. Silicon, while shown to be promising as a lithiumion battery due to its high theoretical capacity, has demonstrated a lack of ability to store sufficient amounts of sodium.4,5 Of all the potential alloy anode materials, Sn (847 mA h g⁻¹) and Sb (660 mA h g⁻¹) have been heavily studied due to their large theoretical capacities. Intermetallic alloys, like SnSb, have smaller volume expansions upon sodiation, resulting in longer cycle life and improved rate performances. Previous reports on SnSb have suggested that polycrystalline SnSb reforms upon cycling in lithium-ion batteries, which may have some benefits in terms of its mechanical properties.6 Due to the inability to directly transfer knowledge of anode research from lithium-ion to sodium-ion technology, i.e. Si and graphite, SnSb has become a frontrunner for potential application as a sodium-ion battery anode. Ultimately, our goal is to develop an easy and scalable synthesis method with control over the composition, morphology, and surface area of the SnSb anode material, while enhancing its performance.

The bimetallic SnSb alloy has been previously synthesized using methods such as ball milling, electrospinning, hot injection, chemical reduction, solvothermal, and through traditional solid-state means.^{6–11} Most of these methods require higher temperatures, which can cause heterogeneous products given the difference in vapor pressure between the two elements. All of these synthetic methods produce powders as their product, resulting in the need for binders for testing the active materials electrochemically in a battery. Here we directly electrodeposit SnSb is onto a conducting substrate at room temperature, without the need of additional binders or post processing. Electrodeposition enables control of the composition, particle size, and thickness of the material. While the first Sn–Sb lithium anode reported was synthesized via electrodeposition, pure phase SnSb has never been reported through this process.^{12–17} The most common impurities in previous reports are Sn, Cu₂Sb, Cu₃Sn, and SnO. All of these impurities are electrochemically active. As a result, the electrodeposition of pure phase SnSb is desired in order to study how the pure phase material interacts with other components in the battery during electrochemical cycling.

In this study, we have successfully synthesized pure phase SnSb by electrodeposition by using a deep eutectic solvent. Pure SnSb electrodes exhibit competitive gravimetric capacities compared to carbon with binder additives, while maintaining long cycle life in a sodium-ion battery.

3.3 Experimental Section

3.3.1 Cyclic voltammetry and electrodeposition of SnSb from ethaline solution

Pure phased SnSb (1:1 ratio; verified by X-ray diffraction (XRD) and energy dispersive Xray spectroscopy (EDS)) electrodes were prepared by single-step electrodeposition process using a three-electrode setup. A platinum working electrode (BASi, 1.6mm diameter), a platinum mesh counter electrode (100 mesh, Alfa Aesar), and silver wire reference electrode were used for cyclic voltammetry. Cyclic voltammetry was done at a rate of 50 mV·s⁻¹. A similar setup consisting of nickel foil (Sigma Aldrich) working electrode, a platinum mesh counter electrode, and silver wire reference electrode were used for the electrodeposition process. An ethaline solution, consisting of 1:2 molar ratio of choline chloride (VWR, High Purity) and ethylene glycol (Fisher Scientific), respectively, was used as the electrodeposition solvent. 50 mM SbCl₃ (Sigma Aldrich, ACS reagent) and 50 mM SnCl₂·2H₂O (Sigma Aldrich, ACS reagent) were dissolved into the ethaline to form the deposition solution. Electrodepositions were performed at 25° C with a constant potential of -0.7 V vs Ag/Ag⁺.

3.3.2 Electrochemical testing of electrodeposited SnSb

Electrochemical testing was performed in a Swagelok half-cell. The half-cell contains a SnSb electrodeposited onto Ni foil, polypropylene separator (MTI Corp) and glass filter (Whatman) filled with 1 M NaPF₆ (Strem Chemicals) in dimethyl carbonate (DMC) (Sigma Aldrich, anhydrous) + 5% by volume fluoroethylene carbonate (FEC) (Sigma Aldrich), and sodium metal (Sigma Aldrich). Half cells were electrochemically tested with an Arbin battery tester (BT-2000). C-rate was determined based on theoretical capacity of each electrode.

3.3.3 Materials Characterization

The surface morphology and composition were examined by scanning electron microscopy (SEM) (JOEL JSM-6500F operating at 15 kV) and EDS (Oxford Instrument X-Max). The EDS spectra were analyzed using AZtec software (Oxford Instrument). The crystal structure of electrodes were identified by glancing angle X-ray diffraction (GAXRD) (Bruker D8 Discover Series I,Cu K α radiation, λ = 1.54184 Å). *Ex-situ* SEM and *ex-situ* XRD were performed after galvanostatically cycling the SnSb electrodes to different states of charge/discharge after set number of cycles. Electrodes were disassembled in an Argon glovebox and electrodes were cleaned using DMC prior to *ex-situ* studies.

3.4 Discussion and Results

Thin films of SnSb were synthesized using a solution containing Sn(II) and Sb(III) chlorides as precursors, and ethaline(1 : 2 by weight choline chloride to ethylene glycol) was used as the solvent for this electrodeposition solution. Cyclic voltammetry of the individual tin and antimony in ethaline solutions (Fig. 3.1a and b) and the solution containing both tin and antimony in ethaline (Fig. 3.1c) were examined in order to identify the potential at which co-electrodeposition of the two metals should occur. The cyclic voltammetry of the solution containing both Sn(II) chloride and Sb(III) chloride in ethaline presents two reduction peaks during its first sweep that can be identified based on the cyclic voltammetry of the individual solutions. During the first cathodic sweep, the reduction of Sb³⁺ to Sb⁰ is present at 0.3 V and reduction of Sn²⁺ to Sn⁰ at 0.55 V vs. Ag/Ag⁺ or the stripping of Sn⁰ into Sn²⁺ and 0.2 V vs. Ag/Ag⁺ for the stripping of Sn⁰ into Sh³⁺ to Sb⁰ at 0.3 V and Sh²⁺ to Sn⁰ at 0.55 V vs. Ag/Ag⁺ for the stripping of Sn⁰ into Sh³⁺ to Sb⁰ at 0.3 V and Sh²⁺ to Sn⁰ at 0.55 V vs. Ag/Ag⁺ are believed to be related to the Sb³⁺/Sb⁵⁺ couple. The reduction of Sh³⁺ to Sb⁰ at 0.3 V and Sh²⁺ to Sn⁰ at 0.55 V vs. Ag/Ag⁺ are the crucial data needed for the electrodeposition of SnSb. Due to tin's more negative reduction potential, co-deposition of Sb and Sn should occur at a potential more negative of 0.55 V vs.



Figure 3.1: Cyclic voltammograms of a) $50 \text{mM} \text{SnCl}_2 \cdot 2H_2\text{O}$ in ethaline and b) $50 \text{mM} \text{SbCl}_3$ in ethaline separately b) $50 \text{mM} \text{SnCl}_2 \cdot 2H_2\text{O}$ and $50 \text{mM} \text{SbCl}_3$ in ethaline combined. An Ag wire reference and Pt working electrode were used at a scan rate of 50 mV/s. d) XRD and e) SEM-EDS verifying the presence of SnSb.

Ag/Ag⁺ . The deposition potential cannot be 0.3 V vs. Ag/Ag⁺ as the cyclic voltammetry data suggests the stripping of Sn occurs while Sb plates between 0.3 V and 0.45 vs. Ag/Ag⁺ . This oxidative current suggesting the stripping of Sn⁰ into Sn²⁺ is not complete until 0.45 V. Using this data, and through optimization of electrodeposition conditions, SnSb was electrodeposited at 0.7 V vs. Ag/Ag⁺ onto a nickel substrate. The X-ray diffraction (XRD) pattern verifies the formation of only SnSb phase onto the nickel substrate (Fig. 3.1d). A nickel substrate was used instead of copper due to possible detrimental migration effects of copper into the active material layer seen in a previous work.¹⁸

The electrochemical performance of the thin film SnSb as a sodium-ion anode was investigated using Swagelok half-cells. A standard electrolyte of 1 M NaPF₆ in dimethyl carbonate (DMC) with 5% by weight fluoroethylene carbonate (FEC) was used for all tested cells. Lifetime cycling studies with greater than 200 cycles are rarely seen in Sn–Sb literature, ^{6,19–23} which does not show the overall performance and failure of the material. As shown by the galvanostatic cycling at C/2 rate, the electrodeposited SnSb has higher stability and better performance than either pure Sn and Sb electrodeposited from ethaline (Fig. S3.1). During its initial discharge, a significant amount of irreversible capacity is observed, which may be related to the formation of a solid-electrolyte interface (SEI) layer between the surface of the electrode and the decomposing electrolyte. However, after the initial cycle, the performance of the material begins to stabilize with a discharge capacity of 548.2 mA h g⁻¹ on its second cycle. Similar to previous reports, the capacity obtained at around the C/2 rate is found to be in the range of 400–600 mA h g⁻¹, which is significantly less than its theoretical capacity (752 mA h g⁻¹). Others have hypothesized that this is due to the inability of tin to sodiate completely in SnSb due to a shift to higher overpotentials at this rate.²⁴ Based on the capacity at the second cycle, electrodeposited SnSb is found to maintain significant stability during cycling (Fig. 3.2) with 95% capacity retention after 300 cycles (at 520.8 mA h g⁻¹) and 90.5% capacity retention after 500 cycles (at 496.1 mA h g⁻¹). The SnSb anode retains this impressive stability over many cycles and does not fall below 80% capacity retention until after 800 cycles. This slow decrease in capacity can be connected to continuous volumetric expansion and pulverization, resulting in isolation of active material and growth of SEI on the newly exposed surface. This growth of the SEI will result in slower kinetics and eventual sudden death of the cell. This can be supported with ex situ SEM images taken of a SnSb electrode after cycling in a sodium-ion half-cell showing a buildup of an organic-like SEI on the electrode surface in later cycles (Fig. S3.2).



Figure 3.2: Electrochemical performance of electrodeposited SnSb (left). The test was performed by galvanostatically cycling at C/2 rate between the potential window of 0.01 V – 1.5V in a sodium half-cell. Rate capability of electrodeposited SnSb at different current rates (right). The test was performed in a sodium half-cell for 8 cycles at each different rate. The potential range used was 0.01 V – 1.5 V.

Rate capability tests were also performed to test the performance of pure SnSb at different current densities (Fig. 3.2). The electrodeposited SnSb exhibits specific gravimetric capacities of 720 mA h g^{-1} , 620 mA h g^{-1} , 540 mA h g^{-1} , 500 mA h g^{-1} , 472 mA h g^{-1} , and 440 mA h g^{-1} at C/10,

C/5, C/2, 1C, 2C, and 4C, respectively. After cycling at the higher rates, a cycle at C/10 rate shows that the electrode fully recovers with no noticeable drop in capacity, which verifies the stability of the electrode.

Using the C/2 rate galvanostatic cycling data, differential capacity plots were extracted for pure Sn, Sb, and SnSb phase samples (Fig. 3.3a–c). Unlike previous reports for SnSb in lithiumion batteries, the electrochemistry involved with the sodiation of SnSb is not just the addition of Sn and Sb sodiation events individually. The sodiation events of SnSb occur at different potentials when compared to the electrodeposited Sn and Sb electrodes individually. Similarly to previous reports,⁹ sodiation events for SnSb are seen at 0.64 V, 0.46 V, and 0.28 V with complementary desodiation events occurring at 0.6 V, 0.8 V, and 0.95 V. The sodiation event seen at ~0.01 V in SnSb when compared to the pure Sn electrode supports the hypothesis from previous reports that the inability of tin to completely sodiate in SnSb may be the reasoning as to why SnSb cannot reach its theoretical capacity at this rate.



Figure 3.3: Differential capacity plots of electrodeposited a) Sb b) Sn and c) SnSb showing the first two cycles. Differential capacity plots of electrodeposited d) SnSb and e) 50:50 Sn:SnSb during the 1st, 2nd, 5th, 10th, 50th, 100th, and 150th cycles. Obtained from galvanostatically cycling at C/2 rate, within the range of 1.5 V – 0.01 V vs Na/Na⁺.

The differential capacity plots also verify the lack of Sn impurity phases present as a result of this synthesis. Fig. 3.3b shows a sodiation event at 0.01 V and a desodiation event at 0.2 V that are sharp and distinct features observed when cycling at this current density in the presence of Sn and not pure phase SnSb. This observation is verified by intentionally introducing Sn impurities in a 50 : 50 Sn : SnSb electrode (Fig. 3.3e), where the differential capacity plot presents the defined desodiation event at 0.2 V that is not present over the different cycles at C/2 of pure phase SnSb (Fig. 3.3d). This suggests introduction of Sn impurities would ultimately increase Sn desodiation activity at 0.2 V to a more defined peak as more Sn is present in this system when cycling at this rate. Galvanostatic cycling of SnSb films containing Sn impurities also suggests that a Sn impurity is the detrimental to the electrode's cycle life (Fig. S3.3).

Interestingly, our ex situ XRD data (Fig. 3.4) shows the reappearance of crystalline SnSb after the first cycle at C/2 rate, which previous reports did not see. Previous literature reported the disappearance of the peaks and the formation of amorphous features immediately after the first cycle.^{24,25} Our work suggests the electrodeposited SnSb does reform, but gradually loses long range order and changes from crystalline SnSb to an amorphous phase with each successive cycle, unlike the immediate transformation observed in previous reports. This observation is similar to what was seen in a previous study of SnSb in lithiumion batteries where SnSb reforms, but loses long range ordering over cycling.⁶ Extended X-ray absorption and fine structure (EXAFS) from a recent report also suggests the reformation of the same SnSb phase with similar Sn and Sb environments after desodiation, but loss of long range ordering based on their data.²⁶ Transmission electron microscopy (TEM) and electron diffraction from a recent study also support SnSb reformation.²⁷ Additional experiments were performed verifying the reformation of crystalline SnSb after electrochemical cycling in our system (Fig. S3.4).

3.5 Conclusion

To summarize, by using an ethaline-based solution the electrodeposition of pure phase SnSb has been reported for the first time. Electrodeposited SnSb, without binders and carbon additives, was tested as a sodium-ion battery anode. While long-term cycling studies over 200 cycles have rarely been previously reported in SnSb literature, we report 1000 cycles to better understand the lifetime and long cycling stability of our SnSb electrodes. Although capacity below theoretical maximum was obtained from galvanostatic cycling at C/2 rate, SnSb exhibited high cycling stability, falling below 80% capacity retained after 800 cycles. Rate capability tests demonstrated the stability of SnSb cycling with higher current densities. Differential capacity plots and ex situ XRD reveal the gradual change, instead of an immediate change as seen from previous reports, from crystalline SnSb to an amorphous phase for electrodeposited SnSb during C/2 cycling. The differential capacity plots also verify the purity of SnSb with absence of distinct Sn electrochemical events. This study reveals some structural integrity with the reformation of SnSb, which may be related to the electrochemical stability seen. If the reformation is important to the stability of the material, purity of the material is crucial for obtaining longer cycle lifetime of the material. The films we report here are thin, but recently, the electrochemical performance of a similar thickness material, ~200 nm Sn, was electrodeposited on a 3D scaffold architecture, and that electrode had triple the areal loading of current slurry-based anodes.²⁸ As new directions like this appear for intermetallic alloys, the SnSb reported here may be useful for implementation in newer 3D architectures. Future studies in better understanding the structural integrity and electrochemistry that occur during cycling of this material may help improve not only the understanding and lifetime of SnSb, but hopefully of all intermetallic alloys that can lead to advancements towards commercialization.



Figure 3.4: Ex-situ XRD of electrodeposited SnSb galvanostatically cycled at C/2 rate, within the range of 1.5 V - 0.01 V vs Na/Na⁺.

3.6 References

- 1. P. Ge and M. Fouletier, *Solid State Ionics*, 1988, **28-30**, 1172-1175.
- 2. M. M. Doeff, Y. Ma, S. J. Visco and L. C. De Jonghe, *J. Electrochem. Soc.*, 1993, **140**, L169-L170.
- 3. D. A. Stevens and J. R. Dahn, J. Electrochem. Soc., 2000, 147, 1271-1273.
- 4. S. Komaba, Y. Matsuura, T. Ishikawa, N. Yabuuchi, W. Murata and S. Kuze, *Electrochem Commun*, 2012, **21**, 65-68.
- 5. C.-H. Lim, T.-Y. Huang, P.-S. Shao, J.-H. Chien, Y.-T. Weng, H.-F. Huang, B. J. Hwang and N.-L. Wu, *Electrochim. Acta*, 2016, **211**, 265-272.
- 6. C. M. Park and H. J. Sohn, *Electrochim. Acta*, 2009, **54**, 6367-6373.
- 7. F. J. Fernandez-Madrigal, P. Lavela, C. P. Vicente and J. L. Tirado, *Chem. Mater.*, 2002, 14, 2962-2968.
- 8. L. G. Xue, X. Xia, T. Tucker, K. Fu, S. Zhang, S. L. Li and X. W. Zhang, *J. Mater. Chem. A*, 2013, **1**, 13807-13813.
- 9. M. Walter, S. Doswald and M. V. Kovalenko, J. Mater. Chem. A, 2016, 4, 7053-7059.
- 10. Y. L. Li, W. Zhang, H. H. Cai, J. W. Wang, X. Z. Ren and P. X. Zhang, *RSC Adv.*, 2015, **5**, 105643-105650.
- 11. L. H. Shi, H. Li, Z. X. Wang, X. J. Huang and L. Q. Chen, *J. Mater. Chem.*, 2001, **11**, 1502-1505.
- 12. J. Yang, M. Winter and J. O. Besenhard, *Solid State Ionics*, 1996, **90**, 281-287.
- 13. J. O. Besenhard, J. Yang and M. Winter, *J. Power Sources*, 1997, **68**, 87-90.
- 14. H. P. Zhao, C. Y. Jiang, X. M. He and J. G. Ren, *J. Power Sources*, 2008, **184**, 532-537.
- 15. H. P. Zhao, G. Zhang, C. Y. Jiang and X. M. He, *Ionics*, 2012, 18, 11-18.
- 16. Q. L. Jiang, D. Z. Hu, M. Q. Jia and R. S. Xue, *Applied Surface Science*, 2014, **321**, 109-115.
- 17. S. Sengupta, A. Patra, M. Akhtar, K. Das, S. B. Majumder and S. Das, *J Alloys Compd.*, 2017, **705**, 290-300.
- 18. R. V. S. M.C.Schulze, A.L. Prieto., J. Mater. Chem. A, 6, 12708-12717
- 19. X. Tang, Y. H. Wei, H. N. Zhang, F. L. Yan, M. Zhuo, C. M. Chen, P. Y. Xiao, J. J. Liang and M. Zhang, *Electrochim. Acta*, 2015, **186**, 223-230.
- 20. X. Tang, F. L. Yan, Y. H. Wei, M. Zhang, T. H. Wang and T. F. Zhang, ACS Appl Mater Interfaces, 2015, **7**, 21890-21897.
- 21. P. Antitomaso, B. Fraisse, M. T. Sougrati, F. Morato-Lallemand, S. Biscaglia, D. Ayme-Perrot, P. Girard and L. Monconduit, *J. Power Sources*, 2016, **325**, 346-350.
- 22. Z. Li, J. Zhang, J. Shu, J. Chen, C. Gong, J. Guo, L. Yu and J. Zhang, *J. Power Sources*, 2018, **381**, 1-7.
- 23. J. Qin, T. Wang, D. Liu, E. Liu, N. Zhao, C. Shi, F. He, L. Ma and C. He, *Adv. Mater.*, 2018, **30**, 1704670.
- 24. L. Baggetto, H. Y. Hah, J. C. Jumas, C. E. Johnson, J. A. Johnson, J. K. Keum, C. A. Bridges and G. M. Veith, *J. Power Sources*, 2014, **267**, 329-336.
- 25. A. Darwiche, M. T. Sougrati, B. Fraisse, L. Stievano and L. Monconduit, *Electrochem Commun*, 2013, **32**, 18-21.
- 26. M. Fehse, M. T. Sougrati, A. Darwiche, V. Gabaudan, C. La Fontaine, L. Monconduit and L. Stievano, *J. Mater. Chem. A*, 2018, **6**, 8724-8734.
- 27. H. Xie, X. Tan, E. J. Luber, B. Olsen, W. P. Kalisvaart, K. L. Jungjohann, D. Mitlin and J. M. Buriak, *ACS Energy Lett*, 2018, **3**, 1670-1676.

28. P. Sun, J. Davis, L. Cao, Z. Jiang, J. B. Cook, H. Ning, J. Liu, S. Kim, F. Fan, R. G. Nuzzo and P. V. Braun, *Energy Storage Materials*, 2019, **17**, 151-156.

CHAPTER 4 – UNDERSTANDING THE KINETIC LIMITATION DURING INSERTION-DEINSERTION OF SODIUM INTO \mbox{SnSb}^4

4.1 Overview

The accessible capacity of SnSb anodes is identified to drastically decrease with increasing current rates. Through a mixture of different electrochemical experiments, the electrochemical event at around 0.4 V vs Na/Na⁺ is found to result in the decrease in accessible capacity at higher rates. Electrochemical impedance spectroscopy helps identify the reasoning to this diffusion limited event, which originates from the earlier formation of sodiated Sb.

4.2 Introduction

Rechargeable batteries have become crucial for modern society and new technologies, with increasing reliance on lithium-ion in the upcoming years. Comparing the recent past and the predicted future, our demand for lithium-ion has increased by almost 5 times in the last 5 years, and is expected to double in the next 5 years.¹ (Based on the graphic from BNEF, 50GWh in 2015, 250 GWh in 2020, and 625 GWh in 2025.) As we pursue longer lasting batteries that allow electric vehicles to travel longer distances, higher energy dense battery materials must be explored and realized in order to be competitive with conventional internal combustion engine vehicles that run on natural gas. Both mass and size of the battery material, and ultimately the battery packs, are crucial for portable applications. Of the researched battery materials and technologies, the next battery breakthrough is believed to most likely come from incremental advancement in anode material research.²⁻⁷ Specifically, the closest to realization is the use of

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intermetallic alloys that are at least twice as energy dense as the current generation of graphite dominant anodes. The successful implementation of intermetallic alloys will not only enhance the energy densities of Li-ion batteries used for portable devices, but also enhance the energy density of alternatives, such as Na-ion batteries, that can be utilized in energy grid storage systems.

The compound SnSb has been studied since the 1990s as a Li-ion anode, and has been shown to be a promising anode due to the material's high energy and stability. This stability is related to the synergistic effect found in SnSb that lessens the volumetric change of the electrode and results in the reformation of SnSb after removal of the alkali ion, when compared to Sn and Sb electrodes in Li and Na systems.⁸⁻¹⁴ SnSb combines the stability found for Sb based electrodes and the higher capacity found for Sn electrodes. It can be both a possible alternative to Silicon and a model high capacity system to study volumetric expansion and different phase changes that are involved.

For the Na-ion system, SnSb has a theoretical gravimetric capacity of 752 mAh/g based on the sodation events of Na₃Sb and Na_{3.75}Sn.¹³⁻¹⁴ With graphite and silicon being poor sodium storage materials, SnSb is one of the highest theoretical energy dense Na-ion anode materials.^{15-¹⁷ Unlike the lithiation/delithiation events of SnSb, where the electrochemical events are the sum of individual Sn and Sb lithiation, the sodiation of SnSb goes through electrochemical events that are clearly distinct from the sum of the individual Sn and Sb sodiation events. Due to these distinct electrochemical events depending on the akali ion used, understanding how the change in structural pathway has an effect on the diffusion of the akali ion may assist in gaining insights to kinetic problems faced in other alloy anode systems.}

Lithium and sodium diffusion is highly important to study in these materials, as slower diffusion at certain early electrochemical events can alter further akali insertion/deinsertion into the system. Ultimately, a change in the material's properties that causes this diffusion limitation is a kinetic limitation problem - a bottleneck that will limit the accessible storage capacity of the material, dictate the current/diffusion rate and lower the material's power density. This kinetic

limitation can be one significant reason why materials never achieve their theoretical capacities under normal operating conditions. Understanding the intrinsic limitation is crucial to designing solutions that will attempt to mitigate the limitations that are discovered.

In this study, we will be looking into identifying electrochemical events during galvanostatic cycling that ultimately hinder the capacity SnSb can access. Electrodeposition will be utilized to remove any additives that may convolute the intrinsic property and help truly understand the limitation of the pure, non-composite material. Previous studies by our group on SnSb have focused on understanding the electrodeposition conditions of SnSb, leading to the first reported phased pure SnSb through electrodeposition.^{12, 18} The ability to create this phased pure SnSb is crucial to the material's stability, as our previous reports found impure Sn-rich SnSb in the synthesis lessen the electrode's cyclability in Li and Na cells. Using different electrochemical techniques and analysis, including looking into differential capacity plots and electrochemical impedance spectroscopy (EIS) on the electrodeposited phased pure SnSb electrodes, we are able to identify a kinetic limitation related to an early structural change during sodiation of SnSb that is not found present during lithium testing.

4.3 Experimental Methods

The synthesis and electrochemical methods are similar to those of our previous papers.^{12,} ¹⁸ The electrodeposition of SnSb was performed using the Chi 660C Potentiostat (CH Instrument) and a three electrode setup consisting of nickel foil (Sigma Aldrich) working electrode, a platinum mesh (100 mesh, Alfa Aesar) counter electrode, and silver wire reference electrode. The electrodeposition solution used contains 50 mM SbCl₃ (Sigma Aldrich, ACS reagent) and 50 mM SnCl₂·2H₂O (Sigma Aldrich, ACS reagent) dissolved into an ethaline solution. The ethaline solution consists of 1:2 molar ratio of choline chloride (VWR, High Purity) and ethylene glycol (Fisher Scientific), respectively. The deposition solution was heated at 110° C to remove water in the solution prior to electrodeposition. Electrodepositions were performed at room temperature with a constant potential of -0.7 V vs Ag/Ag⁺. Sn and Sb electrodepositions were performed in similar manner as previously described using 50 mM SnCl₂·2H₂O in ethaline and 50 mM SbCl₃ in ethaline, respectively.

Electrochemical testing of SnSb as an anode for lithium- and sodium- ion battery was performed in a half-cell configuration. Swagelok cells with PFA $\frac{1}{2}$ " straight tube fittings were used for the rate capability tests and CR2025 coin cells were used for impedance studies. The half-cells were assembled consisting of SnSb working electrode, a separator layer consisting of polypropylene separator (MTI Corp) and glass filter (Whatman, Grade GF/A, 21mm), and lithium or sodium metal (Sigma Aldrich) counter electrode depending on experiment. The electrolyte used for these experiments consist of 1.0 M LiPF₆ in dimethyl carbonate (DMC) (Sigma Aldrich, battery grade) + 5% by volume vinylene carbonate (Sigma Aldrich) for lithium testing, and 1 M NaPF₆ (Strem Chemicals) in DMC + 5% by volume fluoroethylene carbonate (FEC) (Sigma Aldrich) for sodium testing. Galvanostatic cycling of the battery were performed on Arbin battery testers (BT-2143 and LBT20084). The C-rates mentioned were determined based on the theoretical capacity of the active material (824 mAh/g for SnSb vs Li, 752 mAh/g for SnSb vs Na). Electrochemical tests were performed with full depth of discharge (0.01 V to 1.5 V vs respective metal) unless otherwise stated.

Electrochemical Impedance Spectroscopy (EIS) was performed at different states of charge/discharge of SnSb. The SnSb were first galvanostatically cycled at C/2 rate to the specific potential, and the potential was held until the current was less than 1 x 10⁻⁹ A, which was when equilibrium was reached. Galvanostatic EIS was performed through a Gamry 1010E potentiostat connected to the Arbin LBT20084 battery tester with a frequency range of 15 kHz to 10 mHz.

In situ X-ray diffraction (XRD) was performed on an electrochemical cell with a Beryllium window made by Laboratoire de Reactivite et Chimie des Solides and as described in a previous paper.¹⁹ Similar to the EIS experiments, the SnSb cell was first galvanostatically cycled at C/2 rate to the specific potentials related to different sodiation/desodiation events of SnSb, and the

potential was held until the current was less than 1 x 10⁻⁹ A, which was when equilibrium was reached. The Bruker D8 Discover DaVinci X-ray diffractometer (Cu K α radiation, λ = 1.54184 Å) was utilized for all of the XRD data presented to identify the crystallinity and presence of different crystalline products. The configuration of the cell and the diffraction peaks unrelated to the active material are presented in the supplementary (figure S4.10).

4.4 Discussion and Results

Rate capability tests performed on SnSb as an anode in the lithium- and sodium- ion system reveal differences in capacity retention with increasing rates depending on the alkali system studied (figure 4.1). Galvanostatic lifetime cycling of the electrodeposited SnSb used in this study was reviewed and discussed in previous studies.¹² Rate capability tests allow for identification of capacity loss related to rate, which can either be due to electrolyte decomposition, intrinsic limitations from the active material, or mechanical instability resulting in loss of electrical contact of the active material. Cycling at different current rates identifies the amount of capacity a material can retain at the different applied currents, and it is typically expected for materials to decrease in specific capacity with increasing rates. As shown in figure 4.1, SnSb vs Na/Na⁺ was cycled at rates ranging from C/10 to 4C while SnSb vs Li/Li+ was cycled at a faster range of rates between C/2 and 20C. Even with higher rate cycling, SnSb performance in a lithium half-cell presented minor specific capacity change between the current rates with 695 mAh/g at C/2 rate and approximately 600 mAh/g at 20C rate. In contrast, the specific capacity of SnSb cycled in a sodium half-cell significantly decreases with the increase of current rate from around 720 mAh/g at C/10 rate to 440 mAh/g at 4C, which is about a 40 percent decrease in accessible capacity of the material. This significant capacity loss signifies either a change of the material's intrinsic properties or a formation of a layer on the surface of the electrode that is limiting sodium ion diffusion into the active material. Returning to the slowest rate of C/10 after 4C rate identifies the significant decrease in rate is not due to mechanical pulverization causing loss of electrical

contact. Differential capacity versus potential plots in a later section will suggest this loss is also not related to a formation of a resistive solid-electrolyte interface on the surface of the electrode, and thus is ultimately due to the material's intrinsic property during sodiation.



Figure 4.1: Galvanostatic rate capability test of SnSb at different C rates.

In order to further identify the cause of the significant decrease of capacity with higher rates, differential capacity plots are utilized to identify any changes in the electrochemistry. Similar to a cyclic voltammogram, the differential capacity plot (or dQ/dV plot) is another analysis method that identifies the potential of different electrochemical events based on when the onset of capacity occurs. The dQ/dV plots compliment the rate capability tests by identifying the specific electrochemical potential at which the capacity loss is found with the change in rate. The dQ/dV plot not only helps relate the loss of capacity to specific events, but also identifies changes in potential related to increased polarization. Changes to the active material can also be identified if capacity is located at different potentials that were not present at earlier cycles. From the dQ/dV

plots of SnSb cycled in lithium (figure 4.2a), we observe the expected combination of the electrochemical features related to the individual lithiation reactions commonly found for Sb and Sn.^{10, 20} The lithiation and delithiation events have been previously identified to be related to Sb at potentials above 0.8 V and related to Sn at potentials below 0.8 V. In contrast, the dQ/dV plot of SnSb cycled against sodium (figure 4.2b) resulted in a new set of peaks different from the sum of the electrochemical events of solely Sn and solely Sb electrodes.¹² Multiple studies have been performed suggesting the sodiation of Sb occurs at more positive potential (above 0.5 V based on figure 4.2b) while sodiation events related to Sn occurs at later potentials (below 0.4 V).²¹⁻²³



Figure 4.2: Galvanostatic cycling of SnSb versus lithium and sodium. dQ/dV plots of SnSb extrapolated from the rate capability test at specific rates a) versus Li, and b) vs Na.

Comparing the dQ/dV plot at different rates, for both systems we identified a slight increase in overpotential with increasing rates that shows the expected dependence of charge transfer with respect to rate. The Butler-Volmer equation and the more simplified Tafel equation,

depict this expected overpotential as the rate increases. At the highest overpotential event for SnSb in a lithium half-cell, minimal potential change, of 0.084 V, is observed as the rate increases from C/2 to 20C, corresponding to the delithiation of Sn at around 0.68 V vs Li/Li⁺. However, when focusing on identifying the reasoning for the decrease in the capacity of SnSb in the sodium halfcell, the dQ/dV plots with increasing rate reveal significant capacity loss is related to the sodiation event corresponding to Sn that occurs between 0.31 V and 0.1 V. While the sodiation step for Sb was following the previous trend of minor increase in overpotential of 0.083 V with increasing rate, the later sodiation of the Sn resulted in an unusual drastic increase of overpotential of the event with every increasing rate. In conjunction with this capacity loss, we identified a significant shift in overpotential for this event with a difference of 0.21 V between the C/10 rate and the 4C rate. This drastic overpotential is alternatively visualized with a Tafel plot to show the drastic change with rate (figure S4.2). Typically, overpotential is related to the system's need to overcome an "activation barrier". We attribute this overpotential related to the change in rate is due to the properties of the intrinsic material and not a buildup of a resistive solid-electrolyte interface over electrochemical cycling. This is verified through the lack of change in the potential of the different SnSb sodiation/desodiation events when comparing the dQ/dV plots of the initial and final cycling at the slowest rate (Figure S4.1). In order to identify the cause of this drastic overpotential during the sodiation of Sn, the impedance of the SnSb cell was studied at the different states of sodiation and desodiation to observe if the limitation in the SnSb sodiation system is related to a specific electrochemical event.

EIS was performed at different states of sodiation and desodiation to observe any changes in the cell's impedance as it goes through the different electrochemical events. Specific points, based on dQ/dV plots, were selected for EIS prior to alkali ion insertion into SnSb, after alkali insertion into Sb, and after alkali ion insertion into Sn, which occurs after Sb, and its respective alkali deinsertion steps. For SnSb vs Li/Li⁺, EIS measurements were taken prior to cycling, at 0.7 V during lithiation, 0.01V during lithiation, 0.8 V during delithiation, and 1.5V during delithiation to

observe the change with the cells after SnSb events. For SnSb vs Na/Na⁺, EIS measurements were taken prior to cycling, at 0.4 V during sodiation, 0.01V during sodiation, 0.4 V during desodiation and 1.5 V during desodiation. EIS measurements of electrodeposited Sn and Sb of similar loading were also taken to compare to SnSb at the different Li and Na potentials previously mentioned.

The lithium EIS data in figure 4.3 is presenting the Nyquist plots of the SnSb, Sn and Sb electrodes at different states of lithiation and delithiation before and after alkali insertion into Sn. In comparing the change of SnSb, Sn and Sb through the different state of lithiation and delithiation, Sn and SnSb were observed to decrease in impedance with the insertion of lithium. Sb was found to stay with similar impedance throughout the different states of lithiation/delithiation. The Nyquist plot of SnSb cell presented an impedance at about average of the measured impedance found for Sn and Sb electrodes at the same state of lithiation/delithiation, which is expected for the combination of the two individual components' properties at the specific state of lithiation/delithiation.



Figure 4.3: Nyquist plots of EIS measurements taken for SnSb (upper right), Sb (bottom left), and Sn (bottom right) at the different points of interests related to different SnSb lithiation/delithiation events. A Nyquist plot (upper left) comparing SnSb, Sn, and Sb at different potentials related to events prior to Sn lithiation (after Sb lithiation), and after Sn lithiation/delithiation are also presented.

In contrast, EIS of different states of sodiation and desodiation (figure 4.4) suggests the properties of the SnSb cells are strongly dictated by the characteristic of sodiated Sb. When looking at the Sn, Sb, and SnSb electrodes at different states of sodiation and desodiation, again we are able to identify a decrease in impedance as we sodiate. However, as we compare the different states of sodiation and desodiation after 0.4 V, the state after the sodiation of Na-Sb, we identify the impedance within the SnSb cell is no longer at an average impedance in between Sn and Sb at the different states of sodiation and desodiation and desodiation, as observed in the lithiation of SnSb cells. The impedance of the SnSb cell at events below 0.4 V are observed to possess the similar

higher impedance of sodiated Sb at these different potentials. This Sb dominant characteristic of the SnSb cell after the sodiation of Sb suggests the formation of the Na-Sb is hindering the sodium diffusion to Sn during the sodiation events related to Sn. This higher impedance of Na-Sb is hypothesized to greatly limit the diffusion of sodium into the system, ultimately dictating the diffusion rate of sodium into Sn at the more negative potential. Hence, results in the cell's increase of overpotential at the event below 0.4 V vs Na/Na⁺ and the drastic decrease in capacity as the SnSb electrodes attempts to drive sodium diffusion into the system with increasing current rates.



Figure 4.4: Nyquist plots of EIS measurements taken for SnSb (upper right), Sb (bottom left), and Sn (bottom right) at the different points of interests related to different SnSb sodiation/desodiation events. A Nyquist plot (upper left) comparing SnSb, Sn, and Sb at different potentials related to events prior to Sn sodiation (after Sb sodiation), and after Sn sodiation/desodiation are also presented.

Recent literature has suggested similar diffusion problems are occurring during SnSb sodiation. One report has suggested that slower diffusion may be related to an amorphous phase formation they observed experimentally through TEM and guantified the change in diffusion through image analysis.²⁴ Presented in figure 4.5 is in situ XRD of our SnSb electrode cycled against sodium, which supports the previously reported observation where SnSb becomes amorphous as soon as sodiation occurs. Crystalline products are not observed until the material becomes fully desodiated, in which SnSb is found to reform. Our results in this report further identify the kinetic problem related to the amorphous phase mentioned by the previous work by identifying. Through EIS, we identified impedance of the SnSb cell is similar to the impedance of Sb electrode after the sodiation of Sb, suggesting the diffusion problem and higher impedance originates from the formation of Na-Sb and diffusion of sodium through this amorphous Na-Sb. Furthermore, the formation of the impeding Na-Sb may further support observations of another recent study where the segregation of Sn is found after the desodiation of SnSb nanowire in a TEM, as the Sn segregation may be the lowest energy route for sodium diffusion around the impeding Na-Sb.^{22, 25} Ultimately, this suggests the sodiation of Sb is a kinetic barrier for insertion of later events found in SnSb, making this step the kinetic limitation for sodium insertion and access to the higher capacities of Sn.



Figure 4.5: In situ XRD of SnSb in an electrochemical cell cycled to the different potentials of interests related to different SnSb sodiation/desodiation events are presented. The peaks labeled by (#) are related to diffraction related to the electrochemical cell (figure S4.9).

4.5 Conclusion

In this report we were able to identify, through a mixture of analysis, the diffusion limiting process found during the sodiation of SnSb. We are able to describe through experimental methods that the limiting process is believed to be due to the sodiation of Sb, where through EIS this was clearly identified to be the state of sodiation at which impedance increases in the SnSb system. Instead of the impedance of the SnSb being at the middle ground between Sn and Sb at the specific state of sodiation, we found the impedance of SnSb greatly resembles that of Sb after Sb sodiation, and continues to be similar in impedance to a Sb cell at the lower potentials. This suggests Sb sodiation becomes the kinetic limitation of sodium diffusion into the SnSb system, dictating the diffusion of sodium into Sn. Ultimately, in order to design ways to improve the limited ionic diffusion into Sn found in SnSb during sodiation, further studies should be focused on understanding the amorphous phase of Na-Sb that is limiting the SnSb system. While studies in literature have already previously investigated on the sodiation of Sb, the structure-kinetic relationship has yet to be well identified.²⁵⁻²⁹ Sb undergoes multiple phase changes, including amorphization, and identifying and characterizing the different phases' properties, electronic and ionic, is required for identifying the problem related to sodium diffusion through Na-Sb. Better understanding Sb present in the SnSb system and also in identifying the specific sodiation structures that occur in pure Sb is a key step moving forward. Identification of the problem is crucial in devising the future solutions for the problem.

4.6 References

1. BloombergNEF *Electric Vehicle Outlook 2020*; Bloomberg Finance L.P.: 2020.

2. Huggins, R. A., Lithium alloy negative electrodes. J. Power Sources 1999, 81-82, 13-19.

3. Larcher, D.; Beattie, S.; Morcrette, M.; Edström, K.; Jumas, J.-C.; Tarascon, J.-M., Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries. *J. Mater. Chem.* **2007**, *17* (36), 3759-3772.

4. Park, C.-M.; Kim, J.-H.; Kim, H.; Sohn, H.-J., Li-alloy based anode materials for Li secondary batteries. *Chemical Society Reviews* **2010**, *39* (8), 3115-3141.

5. Zhang, W.-J., Lithium insertion/extraction mechanism in alloy anodes for lithium-ion batteries. *J. Power Sources* **2011**, *196* (3), 877-885.

6. McDowell, M. T.; Lee, S. W.; Nix, W. D.; Cui, Y., 25th Anniversary Article: Understanding the Lithiation of Silicon and Other Alloying Anodes for Lithium-Ion Batteries. *Adv. Mater.* **2013**, *25* (36), 4966-4985.

7. Zhang, W.-J., A review of the electrochemical performance of alloy anodes for lithiumion batteries. *J. Power Sources* **2011**, *196* (1), 13-24.

8. Besenhard, J. O.; Yang, J.; Winter, M., Will advanced lithium-alloy anodes have a chance in lithium-ion batteries? *J. Power Sources* **1997**, *68* (1), 87-90.

9. Yang, J.; Winter, M.; Besenhard, J. O., Small particle size multiphase Li-alloy anodes for lithium-ion-batteries. *Solid State Ionics* **1996**, *90* (1-4), 281-287.

10. Park, C. M.; Sohn, H. J., A mechano- and electrochemically controlled SnSb/C nanocomposite for rechargeable Li-ion batteries. *Electrochim. Acta* **2009**, *54* (26), 6367-6373.

11. Kalisvaart, W. P.; Xie, H.; Olsen, B. C.; Luber, E. J.; Buriak, J. M., Understanding the Mechanism of Enhanced Cycling Stability in Sn–Sb Composite Na-Ion Battery Anodes: Operando Alloying and Diffusion Barriers. *ACS Applied Energy Materials* **2019**, *2* (7), 5133-5139.

12. Ma, J.; Prieto, A. L., Electrodeposition of Pure Phase SnSb Exhibiting High Stability as a Sodium-Ion Battery Anode. *Chem Commun* **2019**.

13. He, M.; Walter, M.; Kravchyk, K. V.; Erni, R.; Widmer, R.; Kovalenko, M. V., Monodisperse SnSb nanocrystals for Li-ion and Na-ion battery anodes: synergy and dissonance between Sn and Sb. *Nanoscale* **2015**, *7* (2), 455-459.

14. Walter, M.; Doswald, S.; Kovalenko, M. V., Inexpensive colloidal SnSb nanoalloys as efficient anode materials for lithium- and sodium-ion batteries. *J. Mater. Chem. A* **2016**, *4* (18), 7053-7059.

15. Stevens, D. A.; Dahn, J. R., High Capacity Anode Materials for Rechargeable Sodium-Ion Batteries. *J. Electrochem. Soc.* **2000**, *147* (4), 1271-1273.

16. Komaba, S.; Matsuura, Y.; Ishikawa, T.; Yabuuchi, N.; Murata, W.; Kuze, S., Redox reaction of Sn-polyacrylate electrodes in aprotic Na cell. *Electrochem Commun* **2012**, *21*, 65-68. 17. Lim, C.-H.; Huang, T.-Y.; Shao, P.-S.; Chien, J.-H.; Weng, Y.-T.; Huang, H.-F.; Hwang, B. J.; Wu, N.-L., Experimental Study on Sodiation of Amorphous Silicon for Use as Sodium-Ion Battery Anode. *Electrochim. Acta* **2016**, *211*, 265-272.

18. Ma, J.; Prieto, A. L., Understanding The Electrodeposition of Pure Phase Crystalline SnSb from Deep Eutectic Ethaline Solution and Its Application as a Lithium-Ion Anode. *J. Electrochem. Soc.* In submission.

19. Leriche, J. B.; Hamelet, S.; Shu, J.; Morcrette, M.; Masquelier, C.; Ouvrard, G.; Zerrouki, M.; Soudan, P.; Belin, S.; Elkaïm, E.; Baudelet, F., An Electrochemical Cell for Operando Study of Lithium Batteries Using Synchrotron Radiation. *J. Electrochem. Soc.* **2010**, *157* (5), A606.

20. Fernandez-Madrigal, F. J.; Lavela, P.; Vicente, C. P.; Tirado, J. L., X-ray diffraction, Li-7 MAS NMR spectroscopy, and Sn-119 Mossbauer spectroscopy study of SnSb-based electrode materials. *Chem. Mater.* **2002**, *14* (7), 2962-2968.

21. Baggetto, L.; Hah, H. Y.; Jumas, J. C.; Johnson, C. E.; Johnson, J. A.; Keum, J. K.; Bridges, C. A.; Veith, G. M., The reaction mechanism of SnSb and Sb thin film anodes for Naion batteries studied by X-ray diffraction, Sn-119 and Sb-121 Mossbauer spectroscopies. *J. Power Sources* **2014**, *267*, 329-336.

22. Xie, H.; Tan, X.; Luber, E. J.; Olsen, B.; Kalisvaart, W. P.; Jungjohann, K. L.; Mitlin, D.; Buriak, J. M., β-SnSb for Sodium Ion Battery Anodes: Phase Transformations Responsible for Enhanced Cycling Stability Revealed by In-situ TEM. *ACS Energy Lett* **2018**, *3*, 1670-1676.
23. Darwiche, A.; Sougrati, M. T.; Fraisse, B.; Stievano, L.; Monconduit, L., Facile synthesis and long cycle life of SnSb as negative electrode material for Na-ion batteries. *Electrochem Commun* **2013**, *32*, 18-21.

24. Gutiérrez-Kolar, J. S.; Baggetto, L.; Sang, X.; Shin, D.; Yurkiv, V.; Mashayek, F.; Veith, G. M.; Shahbazian-Yassar, R.; Unocic, R. R., Interpreting Electrochemical and Chemical Sodiation Mechanisms and Kinetics in Tin Antimony Battery Anodes Using in Situ Transmission Electron Microscopy and Computational Methods. *ACS Applied Energy Materials* **2019**, *2* (5), 3578-3586.

25. Allan, P. K.; Griffin, J. M.; Darwiche, A.; Borkiewicz, O. J.; Wiaderek, K. M.; Chapman, K. W.; Morris, A. J.; Chupas, P. J.; Monconduit, L.; Grey, C. P., Tracking Sodium-Antimonide Phase Transformations in Sodium-Ion Anodes: Insights from Operando Pair Distribution Function Analysis and Solid-State NMR Spectroscopy. *Journal of the American Chemical Society* **2016**, *138* (7), 2352-2365.

26. Li, Z.; Tan, X.; Li, P.; Kalisvaart, P.; Janish, M. T.; Mook, W. M.; Luber, E. J.; Jungjohann, K. L.; Carter, C. B.; Mitlin, D., Coupling In Situ TEM and Ex Situ Analysis to Understand Heterogeneous Sodiation of Antimony. *Nano Letters* **2015**, *15* (10), 6339-6348.

27. Darwiche, A.; Marino, C.; Sougrati, M. T.; Fraisse, B.; Stievano, L.; Monconduit, L., Better Cycling Performances of Bulk Sb in Na-Ion Batteries Compared to Li-Ion Systems: An Unexpected Electrochemical Mechanism. *Journal of the American Chemical Society* **2012**, *134* (51), 20805-20811.

28. Qian, J.; Chen, Y.; Wu, L.; Cao, Y.; Ai, X.; Yang, H., High capacity Na-storage and superior cyclability of nanocomposite Sb/C anode for Na-ion batteries. *Chem Commun* **2012**, *48* (56), 7070-7072.

29. Baggetto, L.; Ganesh, P.; Sun, C.-N.; Meisner, R. A.; Zawodzinski, T. A.; Veith, G. M., Intrinsic thermodynamic and kinetic properties of Sb electrodes for Li-ion and Na-ion batteries: experiment and theory. *J. Mater. Chem. A* **2013**, *1* (27), 7985-7994.

CHAPTER 5 – UNDERSTANDING THE ELECTRODEPOSITION OF Sn-Sb THROUGH AQUEOUS SOLUTION FOR HIGH MASS LOADING LITHIUM-ION ANODES⁵

5.1 Overview

The electrodeposition of pure crystalline phase SnSb on Ni foam through an aqueous solution is herein reported. This synthesis was successful after carefully mapping the change of the solution pH and electrodeposition parameters that affect the resulting electrodeposited composition and morphology. The electrodeposited SnSb was electrochemically tested as a Lithium-ion anode, with results showing low first cycle initial capacity loss (ICL) as we get closer to 1:1 ratio Sn:Sb (< 5%).

5.2 Introduction

Secondary batteries have emerged as the energy storage technology of choice for a wide variety of applications ranging from portable electronics to electric vehicle market to large energy storage grids for storing excess energy production. Li-ion technologies will be in the forefront, powering portable applications and will be heavily relied on to supply the currently growing market of electric vehicles. Current Li-ion commercial technology utilizes mostly a carbonaceous material, specifically graphite, as the anode of choice.¹⁻² While graphite has been a reliable and cost efficient anode, the material is limited by its overall theoretical capacity, energy density, and rate capability.²⁻³ In order to expand the range of usage for portable technologies, specifically in electric vehicles, new higher energy dense materials must be studied. Currently, silicon is the most studied Li-ion anode candidate, but a full silicon anode has yet to be commercialized after over

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40 years of research due to the material's large volume change during lithiation (420% expansion based on $Li_{4.4}Si$).⁴⁻⁸ Due to this fact, researchers are looking onto studying other energy dense anode materials.

SnSb has been of interest in the Li-ion field due to its high energy density (gravimetric capacity of 824 mAh/g), and lower volume expansion when compared to Si. This slightly lower volume expansion allows for the access to higher capacity, while minimizing volume change. SnSb is one of the most promising anodes in the Na-ion system due to the inability to transfer of what's known from Li-ion batteries. This is apparent with Na-ion anodes, with graphite having minimal capacity for storage due to the larger Na⁺ ion when compared to Li⁺. Silicon, while being a promising anode in Li-ion batteries, has poor storage capability due to the different pathway of storage in Na.⁹⁻¹⁰ While elemental Sn is of interest due to its high capacity, it has typically been reported to have issues with pulverization, resulting in low cyclability.^{2, 11-17} SnSb allows for the utilization of the higher capacity Sn, while shown to have relatively stable capacity retention. SnSb is also believed to have a synergistic effect between Sn and Sb that allows for the reformation of its crystalline form after deinsertion, whether in Li- or in Na-ion system.¹⁸⁻²⁰

SnSb has been synthesized in a wide variety of different techniques.^{18, 21-25} Electrodeposition is of interest due to the ease in the control of composition, thickness, and morphology of targeted materials. This form of synthesis enables for the growth of the material on different pre-templated architectures, allowing the realization of higher surface area 3-D architectures. Ultimately, this technique allows for the synthesis to be easily scalable from benchtop to large scale production. While the first Sn-Sb report as a Li-ion anode was through electrodeposition, the phased pure SnSb, both by crystallinity and atomic composition, was not realized until it was recently reported by our group.²⁶ However, our group further reported the drawback of our synthesis process, as the solvent used is sensitive to humidity and heat, resulting in possibility of impurities or change in targeted composition with longer depositions for higher

mass loadings.²⁷ Due to the limited processability of the synthesis, SnSb electrodeposition through an aqueous solution is desired. Previous outside reports using electrodeposition for Sn-Sb (signifying non-1:1 Sn:Sb) were all through aqueous solution, which all resulted in impurities including crystalline Sn or Sn-rich product present.²⁸⁻³⁴ Although it is not specified whether the authors' attempted the crystalline phase SnSb nor getting close to the 1:1 Sn:Sb atomic ratio, electrodeposition of SnSb has yet to be realized in an aqueous solution and the lack of reports in article and patents suggests this to be possibly challenging. Based on our previous studies, we've found the lifetime of Sn-Sb electrode is greatly dependent on the purity of the material, as composition closer to 1:1 ratio resulted in the best cycle life vs Li and Na. This may be related to the synergistic effect that allows for crystalline SnSb reformation previously stated and others have found have a favorable effect.^{19, 26-27} Through understanding deposition parameters. including solution pH conditions and the electrochemical procedure for the deposition, different compositional products and morphologies were encountered in this report. This understanding of overall parameters allowed us to attempt to successfully synthesize pure SnSb, in terms of crystallinity, on Ni foam. Electrochemical testing of the commercially relevant loading electrodes was performed in Li-ion cell, showing some promising electrochemical metrics.

5.3 Experimental Methods

5.3.1 Preparation of SnSb deposition solution

A 100 mL solution containing 50 mM SbCl₃ (Sigma Aldrich, ACS reagent – 1.1406 g) and 50 mM SnCl₂·2H₂O (Sigma Aldrich, ACS reagent – 1.1283 g), 176 mM Sodium Citrate dihydrate (Fisher Scientific - 5.1612 g), and 400 mM Citric Acid (Sigma Aldrich - 7.6850) were prepared in water. This deposition solution is heated and stirred on a hot plate at 60° C for 5 hours. Depending on the temperature of the room during this heating process, the solution may be translucent or opaque after the 5 hours of heating. Cooler room temperatures result in the more opaque solution. Overall, the solutions become transparent after tuning pH. The solution is then tuned to pH 7.4

(at ~25° C). At about pH of 3.0 - 3.5, the solution becomes clear. During the addition of KOH to increase the pH, the temperature increases by about 20° C. Normally, pH is tuned to about 7.0 (at the higher temperature), and allowed to cooled below 30° C before getting closer to pH of 7.4 (the pH should slightly increase with the lowering of temperature). Varying pH depositions were performed during this study. However, for optimized conditions, pH 7.4 was used due to morphology and XRD. The pH of 7.4 was decided after a study of the depositions at different pH between 6- 8.5 discussed below.

5.3.2 Electrodeposition of SnSb on Ni foam

The electrodeposition was performed in a three electrode setup. The nickel foam (MTI, EQ-bcnf-16m – calendared to ~500-520 µm; foams are 1.0" x 1.5") was first washed by sonicating in a concentrated (~5M) HCl solution for 5 minutes to remove the surface oxide layer. The foam then goes through millapore water and absolute ethanol for 5 mintues each. Ni foam was used to deposit higher mass loading of SnSb. Previous attempts to electrodeposit higher loadings of SnSb on a Ni thin film resulted in the eventual dendritic growth of film with preferred orientation (discussed in 5.4.1). Reference electrode used was a Ag wire, with a type 316 stainless steel (PO# AC-75973470, Elmhurst – 8.5" x 2.25" folded into 2.125" x 2.25" to fit the 150 mL beaker) counter electrode. Electrodeposition solution is placed in a 150 mL beaker and stirred at 100 RPM throughout the depositions. About 1"x 1" of the nickel foam is submerged for the deposition. Depositions were done at room temperature with a pulsing sequence of -0.7 V vs Ag/Ag⁺ for 10 seconds, followed by rest at open circuit potential (0 A) for 15 seconds using a three electrode potentiostat (Gamry 3000 and Gamry 1010 potentiostat). Ideally, the sequence is repeated for 200 cycles, but depending on the overall current passed for the solution, sequence is either shortened or increased. Once deposition is completed, the deposited foam is washed by dipping in water for 2.5 minutes, ethanol for 1 minute, water for 1 minute, and finally ethanol for 1 minute prior to drying.

5.3.3 Cyclic Voltammetry experiments

Cyclic voltammetry experiments were performed in a similar three-electrode setup as previously stated for electrodeposition. Ag wire or standard calomel electrode (SCE) was used as the pseudoreference and reference electrode, respectively. A platinum working electrode (BASi, 1.6mm diameter), and stainless steel counter electrode were used. Cyclic voltammetry was preformed between -1.4 V and 1.0 V vs SCE; -1.0 V and 1.0 V vs Ag/Ag⁺ at a scan rate of 50 mVs⁻¹.

5.3.4 Electrochemical testing

Electrochemical testing were performed on pouch Li half cells. The half cells contain SnSb electrodeposited onto Ni foam, polypropylene separator (MTI Corp), and Li metal. 1 M LiPF6 in ethylene carbonate (EC) and diethyl carbonate (DEC) (50:50 by volume), and 1 M LiPF6 in EC and ethyl methyl carbonate (EMC) (3:7 by volume) + 5% fluoroethylene carbonate (FEC) electrolytes were used in the varying experiments. All cells shown were tested at full range of discharge between 0.01 V and 1.5 V vs Li/Li⁺. C-rate was determined based on theoretical capacity of each electrode.

5.3.5 Materials Characterization

Scanning electron microscope (SEM; JOEL JSM-6500F operating at 15kV) equipped with an energy dispersive x-ray spectroscopy (EDS) x-ray detector (Oxford Instrument X-Max) were used to study the surface morphology and atomic composition throughout the electrodeposited materials studied. The EDS spectra were analyzed and fitted using the AZtec software (Oxford Instrument). The crystallinity and presence of different crystalline products were identified using the Bruker D8 Discover DaVinci x-ray diffractometer (Cu K α radiation, $\lambda = 1.54184$ Å).
5.4 Results and Discussions

5.4.1 Preface to electrodeposition of Sn-Sb from aqueous based-solution: investigations in ethaline solution

Previous investigations on the synthesis of SnSb in a nonaqueous-based solution from our group led to better understanding in the drawbacks of the system, as humidity and heating resulted in changes from the ideal composition.²⁷ Attempts at longer depositions were performed from the nonaqueous ethaline solution, through both constant potential and pulse-rest depositions procedures, that resulted in dendritic growth after the deposition exceeded a certain thickness limit. SEM images revealing the cross-section of depositions are presented, showing the uneven and dendritic growth on the surface of the electro after, at minimum, 380 nm thick film is grown. This may possibly be a result of the change in speciation of the solution through introduction humidity of into the solution over the long deposition times, which makes higher mass loading depositions through ethaline solution not practical. Ideally, the solution should be inert to the ambient environment, which investigating the use through an aqueous solution may be necessary. Another strategy to avoid the dendritic growth at higher thicknesses while maintaining relatively high mass loadings is through electroplating on a higher surface area substrate. Our strategy is to use metal foams as substrates which allows for thinner layers of SnSb, while achieving high mass loadings.

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Figure 5.1: Cross-sectional images of different electrodeposited Sn-Sb from 50 mM $SnCl_2 \cdot 2H_2O$ and 50 mM $SbCl_3$ in ethaline. The following are the sequences used: -0.7 V vs Ag/Ag⁺ for 1800 s (left) and 18 cycles of -0.7 V vs Ag/Ag⁺ for 600 s pulse with 60 s rest (right).

Our previously investigation on the presence of humidity through observing the electrodeposited products from Sn- and Sb- based aqueous solutions may be a useful first step to better understanding electrodeposition conditions of SnSb through an aqueous solution. The XRD patterns provided in figure 5.2 suggest the formation of a product with excess crystalline Sn impurity in conjunction with crystalline SnSb occurs in most acidic pH conditions (i.e., below pH 7). At very basic conditions of pH 8 and above, amorphous products are found. As no basic precursors are involved in the previous ethaline deposition solution, the solution has an acidic pH if water was slowly incorporated over time. However, based on the XRD patterns, a decrease crystalline Sn was observed in the product when the solution pH was between 6 to 8. This pH region with less crystalline Sn suggests a less Sn-rich Sn-Sb is formed and products are closer to the 1:1 Sn:Sb ratio desired.



Figure 5.2: Cyclic voltammetry at 50 mV \cdot s⁻¹ (left) of a 50 mM SnCl₂ \cdot 2H₂O and 50 mM SbCl₃ aqueous solution and its corresponding XRD patterns (right) from electrodeposition performed at -0.7 V vs Ag/Ag⁺ onto Ni foil at varying pH. Figure taken from ref 26.

While the initial deposition sequence was crucial in forming the ideal product (see supplementary), the pH of the electrodeposition solution was found to have a greater effect on the electrodeposition product's morphology and composition.

5.4.2 Effect of solution pH conditions on the electrodeposited morphology and product

The following studies of the solution's pH condition revealed the narrow range at which SnSb forms. At pH below 3.5, the solution is macroscopically translucent, with insoluble white particles visibly dispersed in the solution. As pH of the deposition solution is adjusted with the addition of saturated KOH, the visibility of the white particles originally present causing the translucency of the solution disappears and the solution becomes clear as the pH is adjusted above 3.5. This change in the solution is believe to be related to the complexation of citrate ions with Sn and Sb

(citrate pKa₁=2.92) enabling the dissolution, as we've learned in previous studies in aqueous based solution.³⁵ Based on XRD, electrodeposition from a solution at pH 6 results in the formation of crystalline SnSb and very weak intensity crystalline Sb. SEM images of the deposition product reveal a dendritic morphology on the surface of the electrode, with tree-like growth and branches with a width of about 1 μ m in size. EDS of the dendritic product reveals an atomic composition of 1:2 ratio Sn:Sb is present at this pH.



Figure 5.3: Pulse sequence with -0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. The deposition solution contained 50 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid at pH 6. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for 360 cycles of the pulse sequence.

At the opposite end of the spectrum, electrodeposition from a solution at slightly above pH 8 resulted in a branched growth of the deposition product. However, the morphology of the deposition product at this pH is different from the product found at pH 6, with large, porous voids, containing <500nm thick branches, forming rather than very thick tree-like dendrites. XRD pattern of the deposition product identifies the formation of crystalline SnSb with the presence of a broad hump indicating amorphous products were also formed. Based on atomic composition obtained from EDS, oxides may be forming at these conditions (EDS reveal oxygen ratios >Sn/Sb), which may explain the significant change in morphology and explain the presence of non-crystalline Sn/Sb products present.



Figure 5.4: Pulse sequence with -0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. The deposition solution contained 50 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid at pH 8. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for 360 cycles of the pulse sequence.

At pH 7 solution, the deposition products were found to be more faceted growth and uniform in morphology when compared to the products found at the extremes of our solution range (i.e. pH 6 and 8). Different morphologies were also found depending on the tuning of the solution at this pH (pH 7±0.15). At slightly acidic conditions (pH 6.85), the morphology of the resulting deposition product resembles triangular prism pillars and is found throughout the foam substrate. Based on EDS, the pillar-like morphology has an atomic ratio of 1:2 Sn:Sb and can be used as an indication of Sb-rich Sn-Sb formation. At slight basic conditions (pH 7.15), more faceted crystals, sizes in the range of μ m, are formed near edges of the foam, with non-faceted, nodular growth of particles found away from the edges. The atomic composition of the deposition at this pH also reveal similar 1:2 Sn:Sb atomic ratio of the overall surface, but is revealed to be Sb rich due to the nodular particles found closer to the center of the foam that are more Sb-rich regions. The facets found near the edges of the foam are the desired SnSb product and facets 1:1 Sn:Sb atomic composition.



Figure 5.5: Pulse sequence with -0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. The deposition solution contained 50 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid at pH 7 ±0.15. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for 360 cycles of the pulse sequence at a) slightly basic conditions from pH 7 and b) slightly acidic conditions from pH 7.

Studies of the electrodeposition product performed in a pH 7.22 solution identifies the presence of crystalline facets as a good indicator of 1:1 Sn:Sb. Electrodepositions at this pH resulted in very crystalline µm sized facets present at the edges of the Ni foam. Formation of submicron nodular particles is concurrently present throughout the film in areas away from edges, similar to what was previously found at slightly more basic conditions from pH 7 (±0.15). EDS scans at different regions reveals areas with faceted morphology near the edge of the film has a 45:50 Sn:Sb ratio, while more Sb-rich atomic composition of 1:2 Sn:Sb is found at areas with more nodular and polycrystalline growth away from edges of the foam. The edges are typically believed to be where the presence of facets is more commonly found on the foam due to higher effects of the electric field at edges of the foams, allowing for more even growth. The XRD pattern reveals a product with solely crystalline SnSb, suggesting the richer Sb region detected by EDS must be amorphous.



Figure 5.6: Pulse sequence with – 0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. The deposition solution contained 50 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid at pH 7.22. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for 360 cycles of the pulse sequence.

To further narrow down the targeted solution range at which the desired 1:1 Sn:Sb product forms, electrodepositions were performed using solutions at different pH between 7 and 8. At pH 7.6, pulse depositions on Ni foam resulted more nodular growth throughout the film. This nodular, broccoli crown-like, morphology typically suggests the growth of a highly polycrystalline material where amorphous regions are present. XRD pattern of this foam deposition reveals the formation of crystalline SnSb, Sb, and a broad hump, suggesting amorphous product may be present on the sample. EDS of the film suggests uneven deposition throughout the film, with the Sn:Sb ratio ranging from 1:2 to 45:55.



Figure 5.7: Pulse sequence with – 0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. The deposition solution contained 50 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid at pH 7.6. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for 360 cycles of the pulse sequence.

In order to balance the crystallinity of the product (found closer to pH 7) with even deposition throughout the film while minimizing the amorphous product present (must be lower than pH 7.6), electrodeposition of SnSb was performed at pH 7.4. Based on the SEM images of the electrodeposited surface, more evenly distributed facets were seen present away from edges of the film than any previously studied conditions. The XRD pattern suggests the product is crystalline SnSb with no impurity Sn or Sb present. However, EDS suggest the Sn:Sb ratio is between 2:3 to 3:5 Sn:Sb. Overall, this Sn:Sb ratio is closer to 1:1 than previous depositions at other pH conditions and suggests pH 7.4 may be an candidate to work towards closer to 1:1 deposit SnSb.



Figure 5.8: Pulse sequence with – 0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. The deposition solution contained 50 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid at pH 7.4. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for 360 cycles of the pulse sequence.

The solution condition discussed previously is summarized in figure 5.9a. At both below 6 and above 8, depositions from both solutions results in branch-like growth of the SnSb. At pH 6, a more dendritic deposition is observed, while pH 8 reveals a porous electrode. At pH 7, electrodeposition products resulted in either facet- or pillar- like morphology present, which were identified to relate to different Sn:Sb compositions. To further explore the deposition of the faceted morphology, depositions at a slightly higher pH were performed. While pH of 7.6 shows some crystalline products, depositions above 7 and below 7.6 were found to be the ideal region, with more uniform faceting throughout the film and atomic ratios of the overall deposition closer to 1:1 Sn:Sb. A speciation diagram for citrate, figure 5.9b, was produced with numbers and procedures from previous citrate literature that can help further the reasoning for this ideal deposition pH region and the different morphologies found at other pH.³⁶ This ideal model of different citrate specie concentrations suggests multiple species of citrate are present concurrently in the solution through majority range of pH that can affect the growth and product of the electrodeposition process (hence the dendritic morphology and off-stoichiometric Sn:Sb found below pH 7). Only at above pH of 7 are Cit³⁻ ions the overly majority specie present, which may be the key to the ideal morphology and formation of SnSb desired (formation of faceted and closer to 1:1 Sn:Sb). However, our studies also show the formation of amorphous oxides above pH 8, limiting the upper range of the deposition solution.



Figure 5.9: a) Summary showing SEM images of the Sn-Sb morphology found at different pH using a pulse sequence with -0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest for 360 cycles. b) The ideal concentration of different citrate species present in the solution at different pH is also presented.

5.4.3 Effect of the tuning of electrodeposition sequence on even deposition growth (Pulse-rest stir depositions)

While pH greatly controls morphology of the electrodeposited film formed, uneven deposition throughout the foam still plagues the deposited electrodes at these solution conditions, which leads to ratios of Sn:Sb different from 1:1. At regions where high electric fields are present, i.e. edges of Ni foam, higher rates of even deposition are seen, leading to more faceted growth. Edges and curvatures of the foam have higher electric field, resulting in more even crystalline deposition. However, at regions away from edges and near the center of the metal surface, less faceted and Sb-rich Sn-Sb deposition is seen, suggesting there may be a lower rate of even deposition at these lower electric field regions. In order to attempt for a more even deposition throughout the film, convection is introduced with the intention of maximizing the concentration of evenly distributed adions present near the surface of the film. The hypothesis for the uneven distribution is due to diffusion of specific adions being limited resulting in uneven amounts of Sn:Sb near the surface of the electrode after a specific amount of pulses that leads to uneven deposition that is observed at the areas with lower electric fields. Convection should allow for greater introduction of ions from the bulk layer of the solution the surface of the electrode (the diffusion layer), replenishing the previously limited (Sn) ions.

Initial attempts for even deposition were performed by stirring during the resting period between pulses. The reasoning for this stirring during rest is to allow for replenishing of depleted ions near the surface of the electrode after every pulse without introducing convection to the electrodeposition process. Initial pulse-rest sequences at pH 7.4 resulted in a deposition with similar crystalline morphology, with facets found throughout the electrode. XRD pattern revealed a highly crystalline SnSb product, with minor presence of crystalline Sb. SEM images suggested a more even deposition was formed on the surface, with more crystalline facets found away from the edges of the electrode. EDS of the surface, however, revealed slight difference from the

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crystalline results, with the deposition being Sb rich, in a 2:3 Sn:Sb atomic ratio. This suggests while growth is more even throughout the foam substrate, the deposition of Sn and Sb is still not occurring in an evenly fashion. This uneven deposition may be suggesting either 1) the rate of deposition of Sn and Sb requires tuning of the solution's concentration to allow the similar rate of deposition onto the film or 2) the rate of diffusion for Sn ions from the bulk of the solution to the surface of the electrode may still be limited, requiring higher amounts of convection to drive diffusion.



Figure 5.10: Pulse sequence with – 0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. Stir was applied during the first 5 seconds of rest. The deposition solution contained 50 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for 360 cycles of the pulse sequence.

Attempts to tune the overall deposition product's Sn:Sb ratio closer to 1:1 by increasing the Sn salt concentration in the deposition solution resulted in uneven growth of Sn rich products. Based on pulse depositions with convection during rest from a solution containing 83 mM SnCl₂.2H₂O and 50 mM SbCl₃, even deposition was visible throughout most of the foam, based on SEM images of the surface. However, dendrites were visible at areas of high curvature. Based on XRD, both crystalline SnSb and Sn were present in the product. While the composition of the film is revealed to be close to 1:1 Sn:Sb based on EDS, this presence of crystalline Sn suggests there must be areas of Sn growth (shown with dendrites and XRD) mixed with Sb-rich Sn:Sb present throughout the film. This ultimately results in products close to 1:1 Sn:Sb, but not the homogenous crystalline product desired.



Figure 5.11: Pulse sequence with – 0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. Stir was applied during the first 5 seconds of rest. The deposition solution contained 83 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for 360 cycles of the pulse sequence.

If the limiting factor for Sn deposition is due to the insufficient mobility from the bulk of the solution to the surface of the electrode, higher convection may result in higher Sn content in deposition. In order to increase convection, stir was left on throughout the pulse and rest sequence. Based on constant stir (100 RPM) in conjunction with the pulse rest sequence, a macroscopically uniform electrode was prepared. The electrodeposition from pH 7.4 solution resulted in product with only crystalline SnSb present. SEM images presents a more even surface, with different facets of similar size present throughout the nickel foam. However, the images reveal uncoated, or poorly coated, areas near the edges of the Ni foam. This is resolved with longer deposition and higher loading electrodeposition. EDS reveal a Sn:Sb ratio of 5:4 and a more even product than previous sequence and methods presented.



Figure 5.12: Pulse sequence with -0.7 V vs Ag/Ag⁺ for 10 seconds of pulse and 15 seconds of rest. 100 RPM stir was applied throughout the pulsing sequence. The deposition solution contained 50 mM SnCl₂.2H₂O, 50 mM SbCl₃, 176 mM Sodium Citrate dihydrate, and 400 mM Citric Acid. The SEM images and XRD patterns are of SnSb electrodeposited onto Ni foam for a) 180 cycles and b) 200 cycles using the pulsing sequence.

5.4.4 Electrochemical performance of Sn-Sb foams in a lithium half cell

Electrochemical tests were performed to better understand the cyclibility and lifetime of the Sn-Sb electrodes in Li half cells. Our previous tests with thin film SnSb suggested the formation of pure SnSb was crucial to the stability of the electrode, as excess Sn resulted in pulverization and shorter lifetime. In our current electrochemical tests, different atomic ratio of Sn:Sb samples were prepared and tested. Initial electrochemical tests using Sb rich Sn-Sb electrodes through our synthesis resulted in slightly lowered loss of coulombic efficiency in the initial cycle. Initial capacity loss (ICL) is crucial to better understand for lithium battery testing, as a majority of energy is lost due to side reaction (SEI formation, lithium trapping to name a few) during the first cycle for alloy materials. This is seen in many reports on promising Si, Sn, Sb reports where typically ≥25% ICL is found when comparing the first cycle to the second cycle. ICL is highly unfavorable, as the lithium source becomes limited by cathode loading in full cells, lowering energy density of the overall cell if ICL is high. Presented on Table XX are the ICL of different Sn:Sb ratio electrodes that were tested. Through our synthesis, at even higher Sb ratio of Sn-Sb produced, ICL was shown to be lower than typically seen in most typical alloy reports, with only 12-14% capacity lost in the first cycle. A correlation is also present between the Sn:Sb ratio to the ICL. As we approach a closer composition to 1:1 Sn:Sb, ICL was seen to decrease to about 3%. This may suggest a correlation between Sn:Sb composition to formation of a more stable SEI where lithium is trapped less.

Table 5.1: Different Sn:Sb ratio electrodes synthesized through the different synthesis conditions with their resulting initial capacity loss and second sodiation gravimetric capacities.

Sn:Sb ratio Closer To 1:1		ICL (%) Lower ICL		Gravimetric Capacity (mAh/g)
1:2.58		12.465374		600.1899335
1:2.25		13.2596685		612.6829268
1:1.67		4.6296296		643.5247663
1 : 1 to 1.25 : 1		4.9808429		677.3735387
1 : 1 to 1.25 : 1		3.0612245		679.6588828
1 : 1 to 1.25 : 1	♦	3.3962264		726.1175403

Presented in figure 5.13 is the cycle lifetime of different Sn:Sb electrodes. Sb rich electrodes show stable capacity of ~600mAh/g until at sharp drop in its capacity occurs after 70 cycles. This sudden sharp drop is believed to be related to a sudden loss of contact between active material and the Ni foam current collector. However, there was a correlation between Sn content in the Sb rich Sn-Sb to the stability of the electrode, with higher Sn content (reaching closer to 1:1 Sn:Sb) showing longer stability prior to failure. The electrode closest to 1:1 Sn:Sb reveals promising capacity at initial cycles with capacity of ~650 mAh/g. However, the capacity greatly diminishes over the next 50 cycles, with only 30% of capacity retained at cycle 50.



Figure 5.13: Lifetime of different Sn-Sb cells. a) Percent (%) capacity (based on theoretical gravimetric capacity) versus cycle number of three different Sn-Sb electrodes. The electrodes were of the following Sn:Sb composition: 1 : 1.67 (red), 1 : 2.25 (blue), 1 : 2.58 (green). B) Specific capacity of 1:1 Sn:Sb electrode. The capacity of typical commercial cells was based on literature. ^{2, 37-39}

5.5 Conclusion

In summary, we have developed an aqueous based method to electrodeposit pure crystalline SnSb. While the initial report of SnSb tested as a battery electrode was through electrodeposition, progress has not been made in search for the formation of pure phase crystalline SnSb aside from our ethaline-based synthesis previously reported. All previous reports outside of our group were from aqueous solution and contained impurities; pure crystalline SnSb is crucial to the lifetime of the material. In this report, we tackle the challenge to develop a synthesis of pure phase crystalline SnSb through aqueous solution, and developed fundamental understanding of the solution in attempt to match both morphology and composition of the electrodeposited product to form a favorable battery anode. We found ideal morphology of the

electrodeposited material is found when the solution is tuned in pH between 7-7.6. Atomic ratio of electrode material was brought closer to 1:1 Sn:Sb through tuning of the SnSb electrodeposition procedure. Electrochemical testing of the SnSb electrodes in lithium half cells resulted in initial capacity loss during the first cycle being significantly less (<5%) than normally found present for other reports of intermetallic alloy, like silicon, electrodes tested in literature. Better understanding in the reasoning for the low ICL may not only help make this electrode material a potential candidate as a next generation battery electrode, but also improve other promising alloy materials with their problematic loss of lithium during the first cycle and push other intermetallic materials over the hump for commercialization. The initial electrochemical testing of the SnSb also showed that material's current limitation with capacity retention throughout cycling. We believe this can further be improved by more rigorous control of growth in the future. The cycle lifetime result also suggests the possible failure of the material due a continuous growth of a solid-electrolyte interface that grows with each increasing cycle. Further studies in building a protective coating on the surface of the electrode material may help reduce the growth of this detrimental electrolyte decomposition on the active material surface, and help further the lifetime of the material.

5.6 References

1. Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M., Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nature Energy* **2018**, *3* (4), 267-278.

2. Self, E. C.; Naguib, M.; Ruther, R. E.; McRen, E. C.; Wycisk, R.; Liu, G.; Nanda, J.; Pintauro, P. N., High Areal Capacity Si/LiCoO2 Batteries from Electrospun Composite Fiber Mats. *ChemSusChem* **2017**, *10* (8), 1823-1831.

3. Asenbauer, J.; Eisenmann, T.; Kuenzel, M.; Kazzazi, A.; Chen, Z.; Bresser, D., The success story of graphite as a lithium-ion anode material – fundamentals, remaining challenges, and recent developments including silicon (oxide) composites. *Sustainable Energy & Fuels* **2020**, *4* (11), 5387-5416.

4. Sharma, R. A.; Seefurth, R. N., Thermodynamic Properties of the Lithium-Silicon System. *J. Electrochem. Soc.* **1976**, *123* (12), 1763-1768.

5. Wilson, A. M.; Reimers, J. N.; Fuller, E. W.; Dahn, J. R., Lithium insertion in pyrolyzed siloxane polymers. *Solid State Ionics* **1994**, *74* (3), 249-254.

6. Wilson, A. M.; Way, B. M.; Dahn, J. R.; Buuren, T. v., Nanodispersed silicon in pregraphitic carbons. *Journal of Applied Physics* **1995**, *77* (6), 2363-2369.

7. Wang, C. S.; Wu, G. T.; Zhang, X. B.; Qi, Z. F.; Li, W. Z., Lithium Insertion in Carbon-Silicon Composite Materials Produced by Mechanical Milling. *J. Electrochem. Soc.* **1998**, *145* (8), 2751-2758.

8. Zuo, X.; Zhu, J.; Müller-Buschbaum, P.; Cheng, Y.-J., Silicon based lithium-ion battery anodes: A chronicle perspective review. *Nano Energy* **2017**, *31*, 113-143.

9. Lim, C.-H.; Huang, T.-Y.; Shao, P.-S.; Chien, J.-H.; Weng, Y.-T.; Huang, H.-F.; Hwang, B. J.; Wu, N.-L., Experimental Study on Sodiation of Amorphous Silicon for Use as Sodium-Ion Battery Anode. *Electrochim. Acta* **2016**, *211*, 265-272.

 Komaba, S.; Matsuura, Y.; Ishikawa, T.; Yabuuchi, N.; Murata, W.; Kuze, S., Redox reaction of Sn-polyacrylate electrodes in aprotic Na cell. *Electrochem Commun* **2012**, *21*, 65-68.
 Ying, H.; Han, W.-Q., Metallic Sn-Based Anode Materials: Application in High-

Performance Lithium-Ion and Sodium-Ion Batteries. *Advanced Science* 2017, *4* (11), 1700298.
12. Li, Z.; Ding, J.; Mitlin, D., Tin and Tin Compounds for Sodium Ion Battery Anodes: Phase Transformations and Performance. *Accounts of Chemical Research* 2015, *48* (6), 1657-1665.

13. Li, T.; Gulzar, U.; Bai, X.; Lenocini, M.; Prato, M.; Aifantis, K. E.; Capiglia, C.; Proietti Zaccaria, R., Insight on the Failure Mechanism of Sn Electrodes for Sodium-Ion Batteries: Evidence of Pore Formation during Sodiation and Crack Formation during Desodiation. *ACS Applied Energy Materials* **2019**, *2*(1), 860-866.

14. Palaniselvam, T.; Goktas, M.; Anothumakkool, B.; Sun, Y.-N.; Schmuch, R.; Zhao, L.; Han, B.-H.; Winter, M.; Adelhelm, P., Sodium Storage and Electrode Dynamics of Tin–Carbon Composite Electrodes from Bulk Precursors for Sodium-Ion Batteries. *Advanced Functional Materials* **2019**, *29* (18), 1900790.

15. Farbod, B.; Cui, K.; Kalisvaart, W. P.; Kupsta, M.; Zahiri, B.; Kohandehghan, A.; Lotfabad, E. M.; Li, Z.; Luber, E. J.; Mitlin, D., Anodes for Sodium Ion Batteries Based on Tin-Germanium-Antimony Alloys. *ACS Nano* **2014**, *8* (5), 4415-4429.

16. Stratford, J. M.; Mayo, M.; Allan, P. K.; Pecher, O.; Borkiewicz, O. J.; Wiaderek, K. M.; Chapman, K. W.; Pickard, C. J.; Morris, A. J.; Grey, C. P., Investigating Sodium Storage Mechanisms in Tin Anodes: A Combined Pair Distribution Function Analysis, Density Functional Theory, and Solid-State NMR Approach. *Journal of the American Chemical Society* **2017**, *139* (21), 7273-7286.

17. Jing, W. T.; Yang, C. C.; Jiang, Q., Recent progress on metallic Sn- and Sb-based anodes for sodium-ion batteries. *J. Mater. Chem. A* **2020**, *8* (6), 2913-2933.

Park, C. M.; Sohn, H. J., A mechano- and electrochemically controlled SnSb/C nanocomposite for rechargeable Li-ion batteries. *Electrochim. Acta* **2009**, *54* (26), 6367-6373.
 Kalisvaart, W. P.; Xie, H.; Olsen, B. C.; Luber, E. J.; Buriak, J. M., Understanding the

Mechanism of Enhanced Cycling Stability in Sn–Sb Composite Na-Ion Battery Anodes: Operando Alloying and Diffusion Barriers. *ACS Applied Energy Materials* **2019**, *2* (7), 5133-5139.

20. He, M.; Walter, M.; Kravchyk, K. V.; Erni, R.; Widmer, R.; Kovalenko, M. V., Monodisperse SnSb nanocrystals for Li-ion and Na-ion battery anodes: synergy and dissonance between Sn and Sb. *Nanoscale* **2015**, *7* (2), 455-459.

21. Fernandez-Madrigal, F. J.; Lavela, P.; Vicente, C. P.; Tirado, J. L., X-ray diffraction, Li-7 MAS NMR spectroscopy, and Sn-119 Mossbauer spectroscopy study of SnSb-based electrode materials. *Chem. Mater.* **2002**, *14* (7), 2962-2968.

22. Xue, L. G.; Xia, X.; Tucker, T.; Fu, K.; Zhang, S.; Li, S. L.; Zhang, X. W., A simple method to encapsulate SnSb nanoparticles into hollow carbon nanofibers with superior lithium-ion storage capability. *J. Mater. Chem. A* **2013**, *1* (44), 13807-13813.

23. Walter, M.; Doswald, S.; Kovalenko, M. V., Inexpensive colloidal SnSb nanoalloys as efficient anode materials for lithium- and sodium-ion batteries. *J. Mater. Chem. A* **2016**, *4* (18), 7053-7059.

24. Li, Y. L.; Zhang, W.; Cai, H. H.; Wang, J. W.; Ren, X. Z.; Zhang, P. X., SnSb-ZnO composite materials as high performance anodes for lithium-ion batteries. *RSC Adv.* **2015**, *5* (128), 105643-105650.

Shi, L. H.; Li, H.; Wang, Z. X.; Huang, X. J.; Chen, L. Q., Nano-SnSb alloy deposited on MCMB as an anode material for lithium ion batteries. *J. Mater. Chem.* 2001, *11* (5), 1502-1505.
Ma, J.; Prieto, A. L., Electrodeposition of Pure Phase SnSb Exhibiting High Stability as a Sodium-Ion Battery Anode. *Chem Commun* 2019.

27. Ma, J.; Prieto, A. L., Understanding The Electrodeposition of Pure Phase Crystalline SnSb from Deep Eutectic Ethaline Solution and Its Application as a Lithium-Ion Anode. *J. Electrochem. Soc.* In submission.

28. Yang, J.; Winter, M.; Besenhard, J. O., Small particle size multiphase Li-alloy anodes for lithium-ion-batteries. *Solid State Ionics* **1996**, *90* (1-4), 281-287.

29. Besenhard, J. O.; Yang, J.; Winter, M., Will advanced lithium-alloy anodes have a chance in lithium-ion batteries? *J. Power Sources* **1997**, *68* (1), 87-90.

30. Zhao, H. P.; Jiang, C. Y.; He, X. M.; Ren, J. G., A new process of preparing composite microstructure anode for lithium ion batteries. *J. Power Sources* **2008**, *184* (2), 532-537.

31. Zhao, H. P.; Zhang, G.; Jiang, C. Y.; He, X. M., An electrochemical and structural investigation of porous composite anode materials for LIB. *Ionics* **2012**, *18* (1-2), 11-18.

32. Jiang, Q. L.; Hu, D. Z.; Jia, M. Q.; Xue, R. S., Effect of heat treatment temperature on the electrochemical properties of SnSb-based Cu electrodes for lithium batteries. *Applied Surface Science* **2014**, *321*, 109-115.

33. Sengupta, S.; Patra, A.; Akhtar, M.; Das, K.; Majumder, S. B.; Das, S., 3D microporous Sn-Sb-Ni alloy impregnated Ni foam as high-performance negative electrode for lithium-ion batteries. *J Alloys Compd.* **2017**, *705*, 290-300.

34. Li, J.; Pu, J.; Liu, Z.; Wang, J.; Wu, W.; Zhang, H.; Ma, H., Porous-Nickel-Scaffolded Tin–Antimony Anodes with Enhanced Electrochemical Properties for Li/Na-Ion Batteries. *ACS Appl Mater Interfaces* **2017**, *9* (30), 25250-25256.

35. Mosby, J. M.; Prieto, A. L., Direct Electrodeposition of Cu2Sb for Lithium-Ion Battery Anodes. *Journal of the American Chemical Society* **2008**, *130* (32), 10656-10661.

36. Rode, S.; Henninot, C.; Vallières, C. c.; Matlosz, M., Complexation Chemistry in Copper Plating from Citrate Baths. *J. Electrochem. Soc.* **2004**, *151* (6), C405. 37. Nitta, N.; Yushin, G., High-Capacity Anode Materials for Lithium-Ion Batteries: Choice of Elements and Structures for Active Particles. *Particle & Particle Systems Characterization* **2014**, *31* (3), 317-336.

38. Chae, S.; Choi, S.-H.; Kim, N.; Sung, J.; Cho, J., Integration of Graphite and Silicon Anodes for the Commercialization of High-Energy Lithium-Ion Batteries. *Angewandte Chemie International Edition* **2020**, *59* (1), 110-135.

39. Mo, R.; Tan, X.; Li, F.; Tao, R.; Xu, J.; Kong, D.; Wang, Z.; Xu, B.; Wang, X.; Wang, C.; Li, J.; Peng, Y.; Lu, Y., Tin-graphene tubes as anodes for lithium-ion batteries with high volumetric and gravimetric energy densities. *Nature Communications* **2020**, *11* (1), 1374.

CHAPTER 6 – DEVELOPMENT OF A 3D ARCHITECTURAL DESIGN FOR HIGHER STABILITY ANODE –INVESTIGATION INTO THE ELECTROPOLYMERIZATION OF A POROUS POLYANILINE (PANi) AS A CONDUCTIVE AND MECHANICALLY STABLE BACKBONE⁶

6.1 Overview

The design of 3D architectural electrodes can result in batteries with higher energy densities. However, with the higher surface area of 3D electrodes, more electrolyte decomposition occurs at the surface. In order to enhance the stability of electrodeposited 3D SnSb electrodes, different architectural enhancements were proposed. In this study, the first part of these electrode enhancements, through the addition of polyaniline, was investigated. The presence of light and acid concentration was identified to be crucial to the propagation of the polymerization process.

6.2 Introduction

Lithium-ion batteries have become a hot commodity in producing a wide variety of portable applications, specifically with the increase in demand due to the rise of electric vehicle production. The production of electric vehicles has increased by at least 10-fold in the last decade, leading to the rise of battery production dedicated to this industry.¹ Currently lithium-ion battery technology consists of a graphite anode and a lithium metal oxide cathode.² However, the search for higher energy dense materials has led to research on intermetallic alloys as the anode replacement. While Silicon is expected to replace graphite in next generation lithium-ion battery technology, research must also be performed on other high energy dense materials.³ Other materials may have a combination of electronic and mechanical properties that may be of interest in substituting the conventional lithium cells for certain portable applications (e.g. quick burst of discharge, fast charging, safety, longer lifetime, etc.).

⁶ This chapter is written by Jeffrey Ma with the guidance from Amy L. Prieto. J.M. would like to thank Jacob Schneider (Prieto Group, Colorado State University) for their suggestions in writing this chapter.

Tin antimonide (SnSb) has been of interest due to its high energy density while maintaining a higher potential than graphite, resulting in a slightly different solid electrolyte interface (SEI). The SnSb anode allows researchers to tap into the higher capacity Sn and combine it with the more stable structure of Sb, resulting in higher cycling stability of SnSb. This material has also been studied in our group and showed promising properties that relate to its high rate, and ultimately great initial coulombic efficiency.⁴ While SnSb has been shown to grow well throughout a 3D architecture design, the higher surface area of the material results in more area for decomposing electrolyte to build up, resulting in more drastic and detrimental effects of SEI on the cell's life.⁵⁻⁶ A study on Cu-Sb nanowires has previously highlighted the drastic effect of SEI formation on higher surface area electrodes.⁵ In order to enhance SnSb stability leading to longer lifetime, the design of an architecture to protect the material from electrolyte decomposition is required. Previous research on applying a uniform coating on alloy surfaces was explored to solve this problem.⁷⁻¹¹ While the application of a coating may show immediate improvement, due to intermetallic alloy's requirement for large expansions during lithiation, previous study has shown the eventual instability of the coating that results in cracks and pulverization during expansion, leaving an exposed surface for continuous SEI formation.¹² Due to this second challenge, an architecture must be designed to also allow for alloy expansion.

There have been previous reports in literature of different coating architectures that highlight some designs as ways to protect intermetallic alloys. Typically, these reports detail forming a coating around each individual particle prior to the casting as a composite onto metal substrates. In general, a core-shell consists of a core or the most inner material, and at least one shell layer, consisting of an outer layer outside of the core. Core-shell architectures are used due to at least one of the following properties: 1) introduction of new chemical, electrochemical, or physical properties that benefit the core; 2) protect the core from changes occurring at the core material's surface; 3) help protect the core material's structural connectivity to the rest of the

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system; 4) selectively allow particles or ions from traveling to the core. Of the core-shell designs, research on yolk-shell structures, which are structures where void is left behind between the shell and the core, have shown to have some more success in protecting and prolonging the lifetime of alloy materials when compared to core-shell designs without a void built in.¹³⁻¹⁹ Literature utilizing a yolk-shell design encasing alloys such as Si and Sn report success in allowing the core active material to expand during ion insertion, without changing the overall microstructure and while keeping the shell intact. Patents have also shown other core-shell architectures that may be useful to consider. Sila Nanotechnology has patents revealing different designs of core-shell architecture where a porous core is designed, which allows for inward expansion to alleviate the overall particle expansion and to protect the shell layer's integrity.²⁰

In this report, we hope to incorporate design ideas from core-shell literature on particles to create a protective coating for electrodeposited alloy materials that may allow space for the alloy to expand, while protecting the active material from changes outside of the shell. As shown in figure 6.1, our first proposed design lies between a typical core-shell and the more void space yolk shell designs. Our protective layer will be built around electrodeposited alloy materials on a 3D architecture instead of thin film due to the need to mitigate high stress from volume expansion, while attempting to form a commercially relevant loading of active material. Aside from a protective shell and inner core, a porous conductive layer lies in between them, allowing for fast conduction to the active material while the flexible porous structure allows for the alloy the expand without changing the overall size of the shell.

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Figure 6.1: Proposed 3D architectural design for alloy anode.

The first step of creating the previously mentioned core-shell architecture is herein reported by learning to apply porous, conductive layer on the surface of SnSb. The flexible porous material is needed in this architecture to allow the active alloy space to fill during insertion of alkali ions (i.e. lithiation). This porous material flexes and compresses during the volume expansion of the alloy material that would otherwise stress and pulverize the outer protective layer. The synthesis of the porous, conductive, and flexible layer was successful with the formation of polyaniline (PANi), and the ideal conditions for the creation of this material through electrodeposition are described. It was identified that the formation of a uniform polyaniline is highly dependent on the synthesis conditions during the activation step relating to the acid concentration and the presence of a radical former.

6.3 Experimental Methods

The electrodeposition of SnSb onto Ni foam is prepared as previously reported.⁶ The polymerization of aniline was performed in a 3 electrode setup. Electrodes with only Ni foam

present or SnSb deposited on Ni foam were used as the working electrode for this set of experiments. Silver wire was used as a pseudo reference electrode, while stainless steel mesh was the counter electrode. 0.2 M aniline in water was prepared in presence of HNO₃ or H₂SO₄ acid. The acid: aniline ratio greatly affects the rate of aniline deposition, as discussed in the later sections. Once the constant current or constant potential sequence was completed, the foam was cleaned with water and absolute ethanol. Cyclic voltammetry (CV) was performed using a similar three electrode setup where the working electrode was instead replaced with a platinum working electrode (BASi, 1.6mm diameter) at 50 mV·s⁻¹. All depositions and CV were performed using a Gamry 3000 potentiostat.

The surface morphology was studied using a scanning electron microscope (SEM) to identify the aniline addition onto the working surface. Infrared (IR) spectroscopy was used to verify the production of polyaniline. The presence of crystalline product was identified using the x-ray diffractometer (XRD) Bruker D8 Discover DaVinci (Cu K α radiation, λ = 1.54184 Å).

6.4 Results and Discussion

A coating of polymerized polyaniline can satisfactorily perform as a flexible and conductive interface layer. Previous studies on PANi were performed on a wide variety of applications ranging from applications as an electrochromic material, electrocatalyst, biosensor, and capacitor.²¹⁻³⁵ PANi is known to be an environmentally stable material and has easily tunable electrical conductivity of its chains. The PANI properties are highly dependent on the synthesis parameters and solution used for the synthesis. Electropolymerization of aniline is simple and has previously been shown to form easily on multiple types of surfaces, including non-even surfaces and in the form of a porous matrix, which assisted in the fast buildup of charge on a high surface area material.³⁶ Due to this highly conductive polymer network, polyaniline may be a highly desirable flexible structure that also allows for fast conduction between the electrode surface and the coating.

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Polymerization of aniline was shown be highly dependent on the concentration of acid present in the solution. Low concentration of acid (0.025 M) in the polymerization solution resulted in poorly polymerized surface of the electrode. Even at high currents (50 mA, 0.5" x 1" film) and longer polymerization times, low concentration (0.025 M) of acid results in a low rate of aniline polymerization on the surface and the presence of a porous structure is not found. SEM image of a polymerization performed in a solution of 0.025M H₂SO₄ and 0.2M Aniline at 50 mA for 600s (figure 6.2a) reveals the lack of porous polyaniline structure desired. While the SEM image of the resulting product does not reveal any significant changes other than the presence of an amorphous surface, the successful polymerization of the electrode surface can be identified macroscopically with a change in the color of the electrode surface from a gray surface to a black/green/blue film. At the opposite spectrum, high enough concentration of acid:aniline ratio (1 M of H₂SO₄, 4:1 H⁺:aniline) results in heavily dense formation of porous polyaniline, which not only forms a thick film with porous features slightly visible, but also covers the pores of the initial Ni foam. SEM images of polymerization in a solution containing 1M H₂SO₄ and 0.5M aniline using an oxidative sequence of 0.8 V for 420 seconds (figure 6.2b) and 0.8V for 5 seconds, then 15 seconds rest repeated for 60 cycles (figure 6.2c), reveals the thick growth and deposition of polyaniline, while also revealing this thick growth is a result of continuous growth of the porous aniline building block. The correlation between the acidity (pH) of the solution and the reactivity of aniline (H⁺:aniline ratio) can greatly control the rate of polymerization of aniline and alter the morphology of polyaniline to the desired outcome.


Figure 6.2: SEM images of the resulting polymerization of aniline coating on SnSb coated Ni foam at the following varying H_2SO_4 :aniline conditions a) 0.025M H_2SO_4 and 0.2M Aniline solution 50 mA for 600s, b) 1M H_2SO_4 , 0.5M aniline solution 0.8V for 420 seconds c) 1M H_2SO_4 , 0.5M aniline solution polymerization sequence of 0.8V for 5 seconds, then 15 seconds rest repeated for 60 cycles.

Cyclic voltammetry verifies the dependence of acid concentration on aniline polymerization activity (figure 6.3). Cyclic voltammetry was performed on the solution containing 0.2 M aniline and 0.025M H₂SO₄ which showed very low activity in the solution (figure 6.3a). However, small broad peak is present between 0.3 and 0.8 V vs Ag/Ag⁺ before the solvent breakdown at more positive potentials. This may suggest either no oxidation of aniline is occurring or that very minor amounts of aniline are oxidizing to form the radical. For the solution containing

0.2M aniline in 0.2M H₂SO₄ solution, initial cyclic voltammetry cycles result in low current response and low redox activity from the solution. However as more CV cycles occur, the current drastically increases as presented on figure 6.3b, and a green and eventually black surface is present on the electrode. Previous literature has studied the activity of the aniline solution during the electropolymerization that can assist in identifying the processes present in our solution. The anodic peak between 0.1 V to 0.2 V, with the potential depending on the number of CV cycles performed, is previously identified as the oxidation step of the aniline dimer (paminodiphenylamine) into dimer cation-radicals, which is required for initiating polymerization.³⁷ This peak is also believed to be the same step where the oxidation of leucoemeraldine to emeraldine form of polyaniline occurs.³⁸⁻⁴⁰ An anodic peak present between CV cycles 5 and 17 at 0.4V was also mentioned in the previous literatures to be related to the formation of intermediate degradation products (p-benzoquinone) and the oxidation of said products. This peak does not increase drastically with each cycle, as seen with the anodic peak between 0.1V to 0.2V, and disappears with later cycles of CV scans. This disappearance into the larger anodic event suggests the intermediate degradation products may either be a slow electrochemical degradation process or may not be due to our electrochemical oxidation process at all. Due to the disappearance over time, this process found at 0.4 V may be hypothesized to be related to the breakdown of aniline into impure degradation products over time, resulting in less of this anodic peak being present as the impurities have been consumed. Interestingly, unlike other literature which shows a later conversion of emeraline to pemigraniline form of polyaniline at a more positive potential than 0.4V, no peaks are found present in our solution, showing no potential conversion to the pernigraniline form with our process.^{39, 41} Due to emeraline form being the most oxidized form in our solution based on CV and the desired conductive product, either a positive current or potential below 1 V vs Ag can be utilized to electropolymerize aniline in our process. A constant potential of 0.8 V vs Ag was utilized for the electropolymerization process in the following experiements. This potential was selected to ensure the oxidation of aniline to the radical form.



Figure 6.3: Cyclic voltammetry of the following solutions: a) 0.2 M aniline and 0.025M H_2SO_4 b) 0.2M aniline in 0.2M H_2SO_4 .

While the rate of polymerization can be affected by the acid:aniline present in the solution, the presence of light may also greatly alter the ability of aniline to polymerize. Experiments performed in presence of varying degrees of light resulted in different amounts of polyaniline growth when using the same solution and electrochemical sequence. Using a solution containing 0.2M H₂SO₄ and 0.2M aniline (2:1 H⁺:aniline), experiments were performed with repeated sequence of 0.8V for 5 seconds, then rest for 15 seconds for 150 to 200 cycles. SEM images presented of the product reveal the electropolymerization in a dark room resulted in spotty polymerization of aniline present throughout the electrode with specific areas where heavily polymerized polyaniline is present, while in other areas only strands or even no porous polyaniline structure are present with the SnSb electrode surface still visible (figure 6.4a-b). SEM images of the electropolymerization occurring in indirect light reveals a higher amount of porous polyaniline present throughout the electrode surface, although coverage is uneven with areas of poor growth of polyaniline (figure 6.4c). Interestingly, the introduction to direct light resulted in a more even polymerization throughout the electrode, with the porous polyaniline fully covering the SnSb underneath (figure 6.4d-e). This series of experiments suggests the importance of light on the activation of the initial aniline monomer radical present in the solution. With less exposure to light, less aniline radicals are formed resulting in less polymerization of the porous polyaniline and spotty coverage on the surface. The presence of light is necessary for a sufficiently high rate of polymerization to produce a uniform, porous coating.



Figure 6.4: SEM images of the resulting polymerization of aniline coating on SnSb coated Ni foam at the following conditions showing light plays an important role: a,b) $0.2M H_2SO_4$, 0.2M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 150 cycles with indirect light, c) $0.2M H_2SO_4$, 0.2M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 150 cycles in dark room, d,e) $0.2M H_2SO_4$, 0.2M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 150 cycles in dark room, d,e) $0.2M H_2SO_4$, 0.2M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 150 cycles in dark room, d,e) $0.2M H_2SO_4$, 0.2M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 200 cycles in direct light.

Based on these previous observations, the initial conditions of aniline in the solution greatly dictates the polymerization process. Light was found to be necessary to drive the formation of a radical during oxidation of the monomer and affects the even growth throughout the electrode. However, the rate of polymerization can also be controlled based on the presence of protons in the solution, which the acid concentration dictates. Scheme 1 summarizes the initiation of the aniline radical and the propagation of the polyaniline chain. H⁺ is shown to control the formation of ammonium from amide, which can then radicalize in the presence of light. This stabilized radical in the acid can then form a dimer, which further oxidizes and reacts with other radical monomers and continues the polymerization of the material.

Initiation:



Scheme 1: Steps during the electrochemical polymerization of polyaniline.

Another way to utilize the porous polyaniline to protect volume expanding alloys is to use polyaniline as an electronically conductive within the intermetallic alloy material, which can also provide extra mechanical stability (figure 6.5). Research from our group has previously shown similar architecture with the inclusion of carbon nanotubes strengthening the alloy material's mechanical stability that resulted in prolonged battery cycling life.⁴² In order to grow this desired architecture, PANi was first electrodeposited onto the Ni foam prior to SnSb incorporation (figure

6.6). As shown in SEM images, the growth of PANi was successful on Ni foam with the same desired porous structure (figure 6.6a, c). SnSb was then deposited after this porous structure was developed to fill in between the PANi (figure 6.6b, d). The SEM images show the successful SnSb electrodeposition beneath and throughout the pre-deposited PANi structure. XRD verifies the presence of crystalline products, showing the successful electrodeposition onto the PANi structure (figure 6.6e).



Figure 6.5: Proposed 3D architecture where PANi is utilized as a mechanical backbone for the alloy material.



Figure 6.6: SEM images of a,c) PANi electropolymerized onto Ni foam, and b,d) SnSb electrodeposited onto the previous Ni foam with PANi. The images were taken at x500 magnification (a,b) and at x5000 magnification (c,d). XRD pattern of the SnSb electrodeposited onto Ni with PANi is shown in e).

6.5 Conclusion

In summary, the formation of polyaniline through electrochemical polymerization was studied, where the initial polymerization conditions greatly alter the formation of polyaniline to the desired morphology. The presence of light was found to be required in complement to the oxidation potential/current to form the radical specie of aniline for the initiation of the polymerization. The presence of H⁺ was also found to be a crucial factor to the radical formation, which can limit the amount of ammonium ions converted from amide and the overall rate of formation of polyaniline. This control of reaction rate can determine the thickness of the growth and the morphology produced. Specifically for the morphology, the rate can determine whether there is a uniform coating or porous structure on the surface of the electrode. This formation of polyaniline was also found to maintain the SnSb underneath without any stripping or oxidation seen in the first proposed architecture.

The second proposed architecture showed the successful growth of polyaniline on Ni foam prior to SnSb electrodeposition. The SnSb electrodeposition was found to be successful in growing around and throughout the porous polyaniline, as suggested from SEM images. However there is still room to tune the SnSb formed, as unevenness of the SnSb growth and drastic growth in localized areas are seen. Further tuning the nucleation and growth of the SnSb through the electrodeposition process is necessary for a more even product.

This uneven deposition of SnSb on polyaniline may possibly be related to the process of forming polyaniline. Slight variation of potential throughout the deposition may cause a variation of product formed, resulting in a range of different polyaniline forms. While emeraldine form of polyaniline, with oxidation state being 0.5, is conductive and desired, other forms of polyaniline including leucoemeraldine (n=1) and pernigraniline (n=0), are poor conductors that may also form. Previous work using constant potential reveals the product formed is dependent on the potential at which deposition occurs.²² This varying in conductivity, depending on the form of polyaniline

formed on the surface, may be one factor that results in the unevenness and localized growth of the SnSb as we have presented. Further exploration in better tuning and controlling the oxidation of polyaniline may further improve deposition, conductivity, and stability of the polyaniline made. Additionally, the acid and additives in the solution may further alter the electrical conductivity of the material. Previous theoretical work has suggested the yield of the emeraldine form of polyaniline and overall electrical conductivity may be affected depending on the acid used, where the emeraldine form may increase with decreasing ionic strength of the acid.⁴³

While the step in forming the polyaniline was a step forward towards the formation of the desired core-shell morphology, the next step requiring the formation of the shell layer is extremely difficult. Not only is a coating with desired properties and synthesis method needing to be found, in addition the coating must also not drastically change the layers below. Therefore, no high temperature annealing may occur, as this will greatly change the underlying structure. For the first proposed architecture, the coating must also be formed above the porous structure and not fill the voids left below, which many techniques cannot perform. Ideally, the author suggests the addition of a material to fill the pores prior to the formation of the coating. Once the coating is formed, the layer underneath is etched away either chemically or electrochemically, leaving the desired porous structure. Both architectures proposed may face further problems with excess coating blocking the foam pores during application, which may result in a drop in overall energy density of the produced electrode. Furthermore, electrochemical testing of the 3D architecture is needed to identify the benefits that polyaniline and coating may bring in prolonging the stability and lifetime of the material.

6.6 References

1. *Global long-term passenger vehicle sales by drivetrain*; BloombergNEF: Electric Vehicle Outlook 2019.

2. Blomgren, G. E., The Development and Future of Lithium Ion Batteries. *J. Electrochem. Soc.* **2016**, *164* (1), A5019-A5025.

3. Ding, Y.; Cano, Z. P.; Yu, A.; Lu, J.; Chen, Z., Automotive Li-Ion Batteries: Current Status and Future Perspectives. *Electrochemical Energy Reviews* **2019**, *2* (1), 1-28.

4. Ma, J.; Prieto, A. L., Electrodeposition of Pure Phase SnSb Exhibiting High Stability as a Sodium-Ion Battery Anode. *Chem Commun* **2019**.

5. Jackson, E. D.; Prieto, A. L., Copper Antimonide Nanowire Array Lithium Ion Anodes Stabilized by Electrolyte Additives. *ACS Appl Mater Interfaces* **2016**, *8* (44), 30379-30386.

6. Ma, J.; Korala, L.; Prieto, A. L., Understanding the Electrodeposition of Sn-Sb Through Aqueous Solution For High Mass Loading Lithium-Ion Anodes. *J. Electrochem. Soc.* In submission.

7. Yoshio, M.; Wang, H.; Fukuda, K.; Umeno, T.; Dimov, N.; Ogumi, Z., Carbon-Coated Si as a Lithium-Ion Battery Anode Material. *J. Electrochem. Soc.* **2002**, *149* (12), A1598.

8. Dimov, N.; Kugino, S.; Yoshio, M., Carbon-coated silicon as anode material for lithium ion batteries: advantages and limitations. *Electrochim. Acta* **2003**, *48* (11), 1579-1587.

9. Noh, M.; Kwon, Y.; Lee, H.; Cho, J.; Kim, Y.; Kim, M. G., Amorphous Carbon-Coated Tin Anode Material for Lithium Secondary Battery. *Chem. Mater.* **2005**, *17* (8), 1926-1929.

10. Tang, D.; Yi, R.; Gordin, M. L.; Melnyk, M.; Dai, F.; Chen, S.; Song, J.; Wang, D., Titanium nitride coating to enhance the performance of silicon nanoparticles as a lithium-ion battery anode. *J. Mater. Chem. A* **2014**, *2* (27), 10375-10378.

11. Liu, Q.; Pang, C.; Chen, W.; Rao, Z.; Lu, H.; Xue, L.; Zhang, W., Double Coating of Micron-Sized Silicon by TiN@NC for High-Performance Anode in Lithium-Ion Batteries. *Energy Technology* **2019**, *7* (9), 1900487.

12. McDowell, M. T.; Woo Lee, S.; Wang, C.; Cui, Y., The effect of metallic coatings and crystallinity on the volume expansion of silicon during electrochemical lithiation/delithiation. *Nano Energy* **2012**, *1* (3), 401-410.

13. Li, X.; Xing, Y.; Xu, J.; Deng, Q.; Shao, L.-H., Uniform yolk–shell structured Si–C nanoparticles as a high performance anode material for the Li-ion battery. *Chem Commun* **2020**, *56* (3), 364-367.

14. Liu, N.; Wu, H.; McDowell, M. T.; Yao, Y.; Wang, C.; Cui, Y., A Yolk-Shell Design for Stabilized and Scalable Li-Ion Battery Alloy Anodes. *Nano Letters* **2012**, *12* (6), 3315-3321.

15. Yang, J.; Wang, Y.-X.; Chou, S.-L.; Zhang, R.; Xu, Y.; Fan, J.; Zhang, W.-x.; Kun Liu, H.; Zhao, D.; Xue Dou, S., Yolk-shell silicon-mesoporous carbon anode with compact solid electrolyte interphase film for superior lithium-ion batteries. *Nano Energy* **2015**, *18*, 133-142.

16. Zhang, L.; Wang, C.; Dou, Y.; Cheng, N.; Cui, D.; Du, Y.; Liu, P.; Al-Mamun, M.; Zhang, S.; Zhao, H., A Yolk–Shell Structured Silicon Anode with Superior Conductivity and High Tap Density for Full Lithium-Ion Batteries. *Angewandte Chemie International Edition* **2019**, *58* (26), 8824-8828.

17. Ni, W.; Wang, Y.; Xu, R., Formation of Sn@C Yolk–Shell Nanospheres and Core– Sheath Nanowires for Highly Reversible Lithium Storage. *Particle & Particle Systems Characterization* **2013**, *30* (10), 873-880.

18. Zhang, H.; Huang, X.; Noonan, O.; Zhou, L.; Yu, C., Tailored Yolk–Shell Sn@C Nanoboxes for High-Performance Lithium Storage. *Advanced Functional Materials* **2017**, *27* (8), 1606023.

19. Cao, K.; Li, P.; Zhang, Y.; Chen, T.; Wang, X.; Zhang, S.; Liu, J.; Wang, H., In situ tem investigation on ultrafast reversible lithiation and delithiation cycling of Sn@C yolk-shell nanoparticles as anodes for lithium ion batteries. *Nano Energy* **2017**, *40*, 187-194.

20. Yushin, G. N.; Zdyrko, B.; Jacobs, A. T.; Hantsoo, E. T.; Shelton, A. N.; Berdichevsky, E. M. Multi-shell structures and fabrication methods for battery active materials with expansion properties 2013.

21. Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S., Novel Aromatic Poly(Amine-Imide)s Bearing A Pendent Triphenylamine Group: Synthesis, Thermal, Photophysical,

Electrochemical, and Electrochromic Characteristics. *Macromolecules* **2005**, *38* (2), 307-316. 22. Korent, A.; Žagar Soderžnik, K.; Šturm, S.; Žužek Rožman, K., A Correlative Study of Polyaniline Electropolymerization and its Electrochromic Behavior. *J. Electrochem. Soc.* **2020**, *167* (10), 106504.

23. Gemeay, A. H.; El-Sharkawy, R. G.; Mansour, I. A.; Zaki, A. B., Catalytic activity of polyaniline/MnO2 composites towards the oxidative decolorization of organic dyes. *Applied Catalysis B: Environmental* **2008**, *80* (1), 106-115.

24. Niu, L.; Li, Q.; Wei, F.; Wu, S.; Liu, P.; Cao, X., Electrocatalytic behavior of Pt-modified polyaniline electrode for methanol oxidation: Effect of Pt deposition modes. *J. Electroanal. Chem.* **2005**, *578* (2), 331-337.

25. Li, X.; Wang, D.; Cheng, G.; Luo, Q.; An, J.; Wang, Y., Preparation of polyanilinemodified TiO2 nanoparticles and their photocatalytic activity under visible light illumination. *Applied Catalysis B: Environmental* **2008**, *81* (3), 267-273.

26. Nicolas-Debarnot, D.; Poncin-Epaillard, F., Polyaniline as a new sensitive layer for gas sensors. *Analytica Chimica Acta* **2003**, *475* (1), 1-15.

27. Mérian, T.; Redon, N.; Zujovic, Z.; Stanisavljev, D.; Wojkiewicz, J. L.; Gizdavic-Nikolaidis, M., Ultra sensitive ammonia sensors based on microwave synthesized nanofibrillar polyanilines. *Sensors and Actuators B: Chemical* **2014**, *203*, 626-634.

28. Wojkiewicz, J. L.; Bliznyuk, V. N.; Carquigny, S.; Elkamchi, N.; Redon, N.; Lasri, T.; Pud, A. A.; Reynaud, S., Nanostructured polyaniline-based composites for ppb range ammonia sensing. *Sensors and Actuators B: Chemical* **2011**, *160* (1), 1394-1403.

29. Jin, Z.; Su, Y.; Duan, Y., Development of a polyaniline-based optical ammonia sensor. *Sensors and Actuators B: Chemical* **2001**, *72* (1), 75-79.

30. Kumar, R.; Yadav, B. C., Humidity sensing investigation on nanostructured polyaniline synthesized via chemical polymerization method. *Mater. Lett.* **2016**, *167*, 300-302.

31. Jin, Z.; Su, Y.; Duan, Y., An improved optical pH sensor based on polyaniline. *Sensors and Actuators B: Chemical* **2000**, *71* (1), 118-122.

32. Mello, H. J. N. P. D.; Mulato, M., Optochemical sensors using electrodeposited polyaniline films: Electrical bias enhancement of reflectance response. *Sensors and Actuators B: Chemical* **2015**, *213*, 195-201.

33. Cheng, Q.; Tang, J.; Ma, J.; Zhang, H.; Shinya, N.; Qin, L.-C., Polyaniline-Coated Electro-Etched Carbon Fiber Cloth Electrodes for Supercapacitors. *The Journal of Physical Chemistry C* **2011**, *115* (47), 23584-23590.

34. Wang, H.; Lin, J.; Shen, Z. X., Polyaniline (PANi) based electrode materials for energy storage and conversion. *Journal of Science: Advanced Materials and Devices* **2016**, *1* (3), 225-255.

35. Shen, K.; Ran, F.; Zhang, X.; Liu, C.; Wang, N.; Niu, X.; Liu, Y.; Zhang, D.; Kong, L.; Kang, L.; Chen, S., Supercapacitor electrodes based on nano-polyaniline deposited on hollow carbon spheres derived from cross-linked co-polymers. *Synthetic Metals* **2015**, *209*, 369-376. 36. Dalmolin, C.; Canobre, S. C.; Biaggio, S. R.; Rocha-Filho, R. C.; Bocchi, N.,

Electropolymerization of polyaniline on high surface area carbon substrates. *J. Electroanal. Chem.* **2005**, *578* (1), 9-15.

Yano, J.; Yoshikawa, K.-i.; Kitani, A., Kinetic Study of the Electropolymerization of
Aniline Using Chronoamperometric Techniques. *Analytical Sciences* 1997, *13* (5), 741-746.
Fitriyana; Kurniawan, F., Polyaniline-Invertase-Gold Nanoparticles Modified Gold
Electrode for Sucrose Detection. *Indonesian Journal of Chemistry* 2015, *15*, 226-233.

39. Stilwell, D. E.; Park, S. M., Electrochemistry of Conductive Polymers: V. In Situ Spectroelectrochemical Studies of Polyaniline Films. *J. Electrochem. Soc.* **1989**, *136* (2), 427-433.

40. Shim, Y. B.; Won, M. S.; Park, S. M., Electrochemistry of Conductive Polymers VIII: In Situ Spectroelectrochemical Studies of Polyaniline Growth Mechanisms. *J. Electrochem. Soc.* **1990**, *137* (2), 538-544.

41. Plesu, N.; Kellenberger, A.; Mihali, M.; Vaszilcsin, N., Effect of temperature on the electrochemical synthesis and properties of polyaniline films. *Journal of Non-Crystalline Solids* **2010**, *356* (20), 1081-1088.

42. Schulze, M. C.; Belson, R. M.; Kraynak, L. A.; Prieto, A. L., Electrodeposition of Sb/CNT composite films as anodes for Li- and Na-ion batteries. *Energy Storage Materials* **2020**, *25*, 572-584.

43. Can, M.; Özçiçek Pekmez, N.; Yildiz, A., Theoretical investigation of the proton effect on electropolymerization of aniline. *Polymer* **2003**, *44* (8), 2585-2588.

CHAPTER 7 – ENHANCED PERFORMANCE OF SnSb COMPOSITE ANODES THROUGH THE ADDITION OF SWCNT AND PAN FOR LI-ION BATTERIES⁷

7.1 Overview

The biggest challenges hindering intermetallic alloy anodes, like SnSb, from long lifetimes are related to mechanical issues that lead to pulverization of the material, and continuous growth of a resistive solid-electrolyte interface. Here, we look into the effects of adding single-walled carbon nanotube (SWCNT) and polyacrylonitrile (PAN) on the performance of SnSb. SWCNT is believe to provide additional mechanical stability to alloy active materials while PAN coating resists the continuous growth of a resistive electrolyte decomposition on the surface. The addition of these materials to the electrode composite resulted in better performance and lifetime of the SnSb.

7.2 Introduction

Lithium-ion battery technology has become a necessity in today's society and has found a home in most portable applications. Current cell technology uses a highly oxidative metal oxide cathode paired with highly reducing carbonaceous graphite that has been sufficient for use in most current technology. However, with the rise of vehicle electrification to lessen the reliance on gas, a new demand appears in search for higher energy dense batteries. The US Department of Energy develops roadmaps and expectations for energy storage. In order to reach their goal for useable specific energy density of 750 Wh/l in the cell level, we must shift from the use of current technology of graphite to higher energy dense anode materials.¹ While there is innovative research on shifting Silicon into becoming the anode of the next generation of lithium-ion batteries, research has been performed on Silicon for at least the last 30 years and a full silicon anode has

⁷ This chapter is written by Jeffrey Ma with the guidance from Amy L. Prieto. J.M. would like to thank Kelly Nieto (Prieto Group, Colorado State University) for their suggestions in writing this chapter.

yet to be fulfilled.²⁻⁵ Due to this fact, better understanding of other high energy dense alloy anodes may compete with and also help the development of Si.

Among higher energy dense alloy anodes, Sn and Sb have been heavily studied due to their ability to provide high theoretical capacities of 990 and 660 mAh/g, respectively. Due to the slightly higher operating potentials related to the lithiation of Sn and Sb when compared to graphite, these alloy materials are believed to provide safety from undesired lithium plating while also forming a slightly different solid-electrolyte interface (SEI) layer. SnSb has been of interest as an anode bridging Sn and Sb electrodes. While Sn has higher theoretical capacity for lithium-ion anode materials, lower capacity retention is typically observed due to high volumetric expansion and issues relating to pulverization.⁶⁻⁸ However when combining Sn and Sb to form SnSb, capacity retention has increased while being able to access the slightly higher capacity of Sn. The crystalline SnSb has also been found to reform after lithiation/delithiation, suggesting a strong affinity of the material to reform after large expansion of the material.

The major challenge preventing the use of pure alloy anodes are their large volume changes during lithiation, resulting in the formation of cracks once delithiation completes. The formation of the new cracks introduces newly exposed surface, resulting in the growth of the SEI layer. This continuous growth of SEI with successive cycles, complemented with the possibility of the loss of electrical contact from pulverization, results in uncontrolled capacity fading. One way to mitigate the uncontrolled capacity fading is through the formation of a highly electrically conductive network to allow for electrical and mechanical stability throughout the electrode. Single walled carbon nanotube (SWCNT) was recently used to strengthen the mechanical robustness of high areal loading electrodes of up to 700 µm thick.⁹ Recently, research on coatings has shown improvement in helping increase the lifetime of alloy materials. While inorganic coatings, like Al₂O₃, are found to be effective in specific conditions, problems are encountered when factoring the thickness of this layer to its effectiveness in allowing Li-ion mobility and its mechanical

robustness when used on expanding material.¹⁰⁻¹⁶ Many conductive polymer coatings were found to allow for expansion of its coating while maintaining its integrity (without formation of cracks).¹⁷ Of the specified polymers coating studied, polyacrylonitrile was found effective in allowing lithium mobility through its polymer backbone and maintaining coating rigidity, resulting in continuous protection of the anode material from exposure to decomposing electrolyte and overall increase in anode cell life.¹⁸⁻²⁸

In this study, we are attempting to systematically observe if the addition of SWCNT and polyacrylonitrile has an effect on the lifetime of Sn-Sb (Sn-Sb is used to signify non-1:1 Sn:Sb) electrodes. Analysis of the galvanostatic cycling of the electrodes shows the enhancement of the overall lifetime of the electrode upon the addition of SWCNT. Additionally, the rate test of the Sn-Sb/SWCNT/cPAN electrode was performed to clarify how these additives enhance the mechanical and electrochemical stability of Sn-Sb. Differential capacity analysis helps identify changes that occur related to different composite makeup and at different rate conditions.

7.3 Experimental Methods

7.3.1 Synthesis of the SnSb composite electrodes

Powdered Sn-Sb was prepared through co-reduction reaction. First, a solution was prepared containing 250 mM SbCl₃ (Sigma Aldrich, ACS reagent), 250 mM SnCl₂ · 2H₂O (Sigma Aldrich, ACS reagent), and 3 M Sodium Citrate (Fisher Scientific, Certified) in water. The solution was heated and stirred at 60° C until the salts fully dissolved into the solution. This solution was then poured slowly into a second solution containing 1 M NaBH₄ (Sigma Aldrich, powder, reagent grade, \geq 98.5%) and 1 M NaOH(Fisher Scientific, ACS certified) in water, resulting in an exothermic reaction. The dark gray/black precipitate formed in the solution was then filtered through a funnel with vacuum filtration, washed with water, then 0.35M HCI (Fisher Scientific, ACS certified), acetone, and isopropanol. The solid obtained from the filtration was then dried at

100°C in a vacuum oven overnight. Electrodes were prepared using the appropriate amounts of additives needed.

Composite electrodes comprised of a mixture of additives including Super-P carbon black (99+%, Alfa Aesar), polyvinylidene fluoride (PVDF, Kynar HSV 1800), N-methyl-pyrrolidinone (ACS reagent, ≥99.0%, Sigma Aldrich), Tuball BATT (0.4% SWCNT/NMP, 2% PVDF Solef 5130 Stabilizer, OCSiAl), and polyacrylonitrile (PAN, average MW 150,000, Sigma Aldrich) were used. Sn-Sb/Super P/PVDF electrodes were made in an 80 : 10 : 10 ratio by weight; Sn-Sb/SWCNT electrodes were prepared in a 100 : 7.5 ratio by weight; Sn-Sb/SWCNT/PAN electrodes were prepared in a 100 : 7.5 : 5 ratio by weight, respectively. The Sn-Sb/Super P/PVDF composite powders were first mixed together using a mortar and pestle. For the Sn-Sb/SWCNT containing composites, appropriate amounts of Sn-Sb were added to specified amounts of Tuball containing the SWNT and stirred overnight. For the Sn-Sb/SWCNT/PAN containing composites, appropriate amounts of Sn-Sb and PAN were mixed by hand for 45 minutes using a mortar and pestle prior to adding to the needed volume of Tuball. Sn-Sb/PAN containing electrodes were made by first hand grinding Sn-Sb with PAN in a 100:5 ratio by weight for 30 minutes using a mortar and pestle, and adding DMF (Sigma Aldrich, ≥99.8%) totaling 2.5 times the mass of the previous powders and mixing overnight. The resulting composite slurries were casted into electrodes with a slurry thickness controlled and kept at 150 µm. Samples were casted onto Cu foil (25 µm, MTI Corp.) and dried in a vacuum oven at 60° C overnight.

7.3.2 Materials Characterization

The presence of the different crystalline structures present in the sample were studied using the Bruker D8 Discover diffractometer (Cu K α radiation, λ = 1.54184 Å). Scanning electron microscope (SEM; JOEL JSM-6500F) equipped with energy dispersive x-ray spectroscopy (EDS) x-ray detector (Oxford Instrument X-Max) were used to provide the surface morphology and

atomic composition of different samples presented. EDS spectras obtained on the samples are analyzed and fitted using AZtec software (Oxford Instrument).

7.3.3 Electrochemical testing of electrodes

Electrochemical testing was performed in a half-cell configuration using 3032 coin cells (parts from MTI Corp.). The half-cell contains the active Sn-Sb electrode, glass filter separator (Whatman) filled with 1 M LiPF₆ in ethylene carbonate: diethyl carbonate (EC:DEC 3:7) (BASF, Selectilyte) + 5% by volume fluoroethylene carbonate (FEC) (Sigma Aldrich), and Lithium metal. Half cells were electrochemically tested with an Arbin battery tester (LBT20084). C-rate was determined based on the theoretical capacity of the active material in each electrode. Galvanostatic EIS was performed through a Gamry 1010E potentiostat connected to the Arbin LBT20084 battery tester with a frequency range of 15 kHz to 10 mHz.

7.4 Results and Discussion

The Sn-Sb used was synthesized through co-reduction of Sn and Sb precursors in the presence of a reducing agent. The dark gray powder formed was analyzed using an XRD and revealed the presence of both crystalline SnSb and Sb. SEM-EDS spectra suggests the Sn:Sb ratio is 1:2 for the sample, verifying the presence of a Sb rich sample as seen in the diffraction pattern. Different slurry casted composite electrodes were prepared to investigate how the addition of SWCNT and PAN to Sn-Sb affects the performance and lifetime of the material when compared to conventional active/super P/PVDF formulation. Samples containing cyclized PAN (cPAN) were prepared due to recent reports suggesting the cyclization of polyacrylonitrile resulted in a system with higher Li⁺ percolation, leading to a more conductive particle surface coating.²⁹ cPAN was formed by annealing the sample at 270° C for 3 hours under Argon atmosphere.²⁸

Initial characterizations of the casted and dried slurry composite electrodes were studied to observe any changes from the initial Sn-Sb power during the electrode formation process. XRD

patterns of the conventional Super P/ PVDF electrode and SWCNT with PAN electrode reveal the similar presence of crystalline SnSb and Sb that existed prior to the electrode casting. However, the composite electrodes containing the addition of SWCNT and SWCNT/cPAN reveal a change in the crystalline product present. The diffraction pattern of the composite electrode containing the addition of SWCNT has the presence of only crystalline SnSb, while the electrode of SWCNT/cPAN has only Sb present. SEM-EDS reveal all samples remain at a 1:2 Sn:Sb, which suggests the variation of crystalline product with each different electrode may be due to amorphization of certain species and possible oxide formation of certain species on the electrode surface during the heating treatment and drying of the casted composite slurries. SEM images of the electrode surface suggest the addition of the SWCNT (from Tuball) resulted in a more uniformed film, as the sizes of the pores left behind after solvent evaporation were smaller than what's found on the surface of the conventional Super P/PVDF formulation. SEM images also reveal no drastic differences between the SWCNT only electrodes when compared to SWCNT/PAN and SWCNT/cPAN electrodes, suggesting our mixing of PAN and SnSb prior to addition into SWCNT resulted in PAN coating the Sn-Sb surfaces, with no formation of evident segregation between the two materials.



Figure 7.1: XRD patterns of the formulated composite electrodes investigated in this study.



Figure 7.2: SEM images of the surface morphology of the following: a) x25,000 magnification of Sn-Sb powder, b,c) SnSb/Super P/PVDF composite electrode, d,e) Sn-Sb/SWCNT composite electrode, f,g) Sn-Sb/SWCNT/PAN composite electrode, h,i) Sn-Sb/SWCNT/cPAN composite electrode. Figures b,d,f, and h are of x500 magnification images; figures c,e,g, and i are of x5,000 magnification images.

The electrochemical performance of the different Sn-Sb composite electrodes was investigated through different sequences of galvanostatic cycling. The dq/dV plots obtained from the first and second cycle of each different composite electrode reveal the difference in contribution to capacity of each lithiation and delithiation event. The dq/dV for the Sn-Sb/SWCNT and Sn-Sb/SWCNT/PAN electrodes were found to have similar electrochemical events that presented sharp and defined peaks for each lithiation/delithiation event that occurs, while the conventional Sn-Sb/Super P/PVDF and Sn-Sb/SWCNT/cPAN electrodes reveal broader events occurring below 0.8 V vs Li/Li⁺. For the Sn-Sb/SWCNT and Sn-Sb/SWCNT/PAN electrodes, lithiation events were found at 0.83 V, 0.64 V, 0.42 V vs Li/Li⁺ with delithiation events occurring at 0.62 V, 0.73 V, 0.79 V, 1.00 V, 1.06 V, and 1.15 V vs Li/Li+. The less intense delithiation events at 1.00 V and 1.15 V are believed to be related to the formation of Cu₂Sb in the electrode.³⁰ For Sn-Sb/Super P/PVDF and Sn-Sb/SWCNT/cPAN electrodes, during the first cycle the lithiation events were found at 0.86 V, 0.80 V and a broad peak at 0.56 V and 0.20 V with delithiation events occurring at 0.47 V (broad) and 1.06 V. During the second cycle, the dq/dV was found identical for the delithiation events, but peaks related to lithiation drastically changed with the lithiation events present at 0.89 V, 0.86 V, 0.83 V, 0.79 V, and a broad event at 0.2 V vs Li/Li+. The key disappearance of a major contribution to capacity from the broad peak present at 0.56 V during the first cycle lithiation was also no longer present in the second cycle lithiation. Based on previous research investigating the individual events, peaks related to the lithiation/delithiation of Sb occurs between 1.1-0.8 V while lithiation/delithiation related to Sn occurs between 0.8-0.4 V vs Li/Li^{+.31} This suggests the missing event from the initial cycle for Sn-Sb/Super P /PVDF and Sn-Sb/SWCNT/cPAN may be related to the lithiation of Sn. We hypothesize the missing event is related to the loss of amorphous Sn loss due to pulverization or SEI inhibiting the Sn cluster's ability to lithiate after the first cycle. Interestingly, the differences in electrochemical events found in the dQ/dV do not have any correlation as to what crystalline products were present based on XRD prior to cycling. However, the presence of only Sb for Sn-Sb/SWCNT/cPAN and the more intense Sb peak in Sn-Sb/Super P/ PVDF, when compared to Sn-Sb/SWCNT and Sn-Sb/SWCNT/PAN, suggests more amorphous Sn or Sn-O must be present as EDS verifies similar

1:2 Sn:Sb on the electrode, and supports our hypothesis of capacity loss related to amorphous Sn loss during the first lithiation of Sn-Sb/ SWCNT/ cPAN and Sn-Sb/ Super P/ PVDF.



Figure 7.3: dQ/dV plots extrapolated from the first two cycles of the different Sn-Sb composite electrodes galvanostatically cycled at C/2 rate.

The long term cycling performances of the different composite electrodes are displayed in figure 7.4. The electrodes were of similar thicknesses (150 µm) and cycled at a C/2 rate. A drastic loss in capacity is found for the SWCNT and PAN containing composites during the first cycle, with low initial coulombic efficiency of 59%, 64%, and 49% for SWCNT, SWCNT/PAN, and SWCNT/cPAN composite electrodes, respectively. The low coulombic efficiency in the initial cycle is consistent with literature, where most alloy materials lose a large amount of energy during the first cycle related to the formation of the initial SEI layer. This huge loss is detrimental in practical operation of lithium-ion full cells, as lithium ions are limited to the amount of cathode material available and any loss results in a decrease in overall energy density of the cell.



Figure 7.4: a) Galvanostatic cycling of the different composite electrodes at C/2 rate. b)The capacity retention and coulombic efficiency of the same electrodes over their electrochemical test.

In the scenario where conventional lithium-ion composite formula containing Sn-Sb/PVDF/Super P was electrochemically tested, the composite was found greatly instable with a coulombic efficiency of 2.9% for the first cycle. The capacity decreased to 1 mAh/g during the second cycle, losing 98% of the initial capacity. This inability for the composite electrode to remain stable may be due to the thickness of the material, and at 150 µm thick the PVDF is unable to

maintain a rigid structure to keep the electrode electrochemically active. Previous research has suggested while PVDF is a common binder for current lithium ion technologies, it has been shown to work poorly with intermetallic alloy materials, including silicon, due to its inability to withstand large volume changes during lithiation and delithiation of an electrode.³²⁻³⁴ A recent study has shown the inclusion of SWCNT increases the mechanical stability of the electrodes, allowing for the casting of thicker composite electrodes and without drastic failure during the volume change when cycling the battery.⁹ The cycle life of the composite electrodes containing SWCNT shows significant increase in stability presented in the cycle life graph with capacity retained and no sudden steep loss in capacity during cycling.

The lifetime of the different Sn-Sb composites presents an average capacity of 850 mAh/g for SWCNT/cPAN, 750 mAh/g for SWCNT/PAN, and 420 mAh/g for SWCNT over the initial 200 cycles. Sn-Sb/cPAN, without the addition of the SWCNT, was found to have an average capacity of 600 mAh/g over the first 100 cycles. While the capacity shows the material's ability to store energy, capacity retention enables clearer visualization of electrode stability over time. Over the initial 30 cycles, SWCNT/cPAN was found to have the lowest capacity retention with 87.8% (cycle 22) at the lowest point, with SWCNT/PAN having the highest capacity retained. However, SWCNT/cPAN was found to increase in capacity retention (up to 91% at cycle 82) with each successive cycle and eventually surpass capacity retained by the other composite electrodes at cycle 100. This initial drop, then rise in capacity retention is hypothesized to be due to the ability to access more active material closer to the core of the Sn-Sb particles due to the continuous volume change with each successive lithiation/delithation process. The capacity retained for cPAN electrode reaches maximum capacity retention by cycle 150 and begins a slight decrease in capacity. SWCNT and SWCNT/PAN electrodes show a similar trend to each other with a slow continuous decrease in capacity after the initial cycle. Interestingly, SWCNT shows a more drastic loss of capacity when comparing to the electrode with the addition of PAN to the composite

electrode (SWCNT/PAN) (with capacity retention found to be 73.8% at 200 cycle for SWCNT and 84.3% at 200 cycle for SWCNT/PAN). This shows a degree of effectiveness of the PAN coating in protecting the active Sn-Sb material over long cycling and may only be decreasing in capacity due to the eventual buildup of a resistive SEI that ultimately limits ion transport with every successive cycle. However, the heat treatment of PAN to form the cyclized PAN resulted in an even greater capacity retention, suggesting the sample containing cPAN has created a more rigid coating that surrounds the Sn-Sb particles that remains intact through the continuous volume expansion during lithiation/delithiation, resulting in the ability to prevent the buildup of the resistive SEI on the Sn-Sb surface. While the PAN/cPAN coating is found to be important in improving coulombic efficiency and the overall capacity retained, SWCNT is still found to have a greater influence on the composite electrode's overall mechanical stability. This is shown with the composite containing only Sn-Sb/cPAN, which showed the active material's ability to remain active in the composite without containing any presence of SWCNT or binder. However, this composite does show a steep loss in capacity after 100 cycles, which suggests the eventual loss of contact of the composite from the current collector and the lack of mechanical stability without SWCNT.



Figure 7.5: a) Rate capability test of Sn-Sb/SWCNT/cPAN composite electrode ranging from 0.1 C to 10 C rate. Potential range of 0.01 V - 1.5 V vs Li/Li⁺. b) dQ/dV plots extrapolated from the different rates in the rate capability test.

Rate capability tests were performed on Sn-Sb/SWCNT/cPAN composite to study the composites' accessible capacity at different current rates. The Sn-Sb/SWCNT/cPAN composite electrode was found to have a capacity of 930 mAh/g, 900 mAh/g, 839 mAh/g, 767 mAh/g, 677 mAh/g, and 529 mAh/g at 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, and 5 C, respectively. This shows the composite electrode's ability to access fast charging rates of up to 5 C, while maintaining high

capacities. The minimal difference between lithiation and delithiation capacities at the different rates also suggests negligible loss of accessible energy stored in the system, where normally the detrimental formation of SEI is more evident at slower rates. This suggests the cPAN coating's effectiveness in creating a protective barrier around the expanding active material and minimizing energy loss related to side reactions. However, the rate test presents the composite's inability to access capacity at the rate of 10 C with a capacity of <1 mAh/g. This inability to access capacity may either be related to the inability for the intrinsic Sn-Sb to store charge at this rate or the PAN coating being the rate limiting step that inhibits the active material from accessing lithium at this rate. The cycling at the slower 0.1 C rate after 10 C shows access to similar 930 mAh/g capacity found during the 0.1 C rate, proving the capacity loss at 10 C is related to a limited lithium diffusion step for a component in the composite electrode, and not due to mechanical pulverization and loss of the active material's electrical contact to the rest of the cell when cycled at the higher rate.

Differential capacity plots of Sn-Sb/SWCNT/cPAN at different C-rates were extrapolated from the rate test. Similar to the first cycle lithiation/delithiation events found in figure 7.5b of Sn-Sb/SWCNT/cPAN, lithiation events were found at 0.85 V and 0.6 V with delithiation events present at 0.64 V, 0.92 V, 1.05 V, and 1.15 V. Delithiation events at 0.92 V and 1.15 V are believed to be related to the migration of Cu from the current collector into the delithiating Sb active material, resulting in the formation of Cu₂Sb within the film. Comparing the differential capacity plots at different rates, the 0.6 V peak during lithiation is only diffusion limited at current density rates 5 C and higher, with an over potential of 0.085 V when comparing the potential for lithiation at 5 C to 2 C. At rates below 5 C, potential related to the lithiation event and area under said peak stayed consistent throughout different rates (0.05 V difference between 0.1 C and 2 C). In contrast, the 0.85 V lithiation peak slowly shifted to higher potentials with decreasing overall capacity related to this electrochemical event (a shift from 0.87 V at 0.1 C to 0.78 V at 5 C). This suggests the events related to Sb lithiation have been diffusion controlled throughout the different rates up to

5C, but the events related to Sn lithiation were limited by the cPAN coating's diffusion limitation beginning at 5 C and above.



Figure 7.6: Nyquist plots from electrochemical impedance spectroscopy measurements for the different composite electrodes tested a) prior to cycling b) after 150 cycles.

Electrochemical impedance spectroscopy was also measured for the different electrodes after different cycles. Figure 7.6 presents the Nyquist plots of the different composite electrodes containing either/both SWCNT, PAN, or cPAN. Prior to cycling, the impedance of all electrodes was similar and high due to the pristine and unpassivated surface present. Interestingly, once the electrodes were cycled for long enough to establish a stable SEI and possibly identify the effects of the SEI, the benefits of each component of the composite are clearly identified. The EIS of the different electrode composites taken after 150 cycles identified the presence of SWCNT resulting in higher impedance with the presence of a bigger semicircle. The SnSb/SWCNT resulted in the

highest impedance, with SnSb exposed directly to the electrolyte and its decomposing products that may continuously grow on newly exposed surface. The electrode with only SnSb/cPAN resulted in the lowest impedance, showing the importance of cPAN coating in preventing SEI growth on SnSb and creating a stable surface. SnSb/SWCNT/cPAN was found to have lower impedance than SnSb/SWCNT/PAN, showing the effectiveness of cyclizing the PAN in strengthening its ability to protect the SnSb surface from further reaction with the SEI. Ultimately, these experiments identified the importance of cPAN in its ability to prevent further SEI growth that would impede alloy materials.

7.5 Conclusion

In summary, the addition of SWCNT and PAN was studied for their effects on protecting against the large volume expansion of Sn-Sb alloy anodes for lithium-ion batteries. The addition of SWCNT and PAN each had different ways in improving the material's stability and lifetime in a lithium-ion cell. The SWCNT was found to greatly improve the mechanical stability of the Sn-Sb electrode and prolonged the material's life by keeping this large volume expanding material in electrical contact. The PAN was found to work as a protective coating, with prolonged lifetime related to its effectiveness in coating the surface of Sn-Sb and preventing it from interacting with the resistive SEI. Alloy materials typically increased in SEI growth with each cycle due to newly exposed surface, but the coating was found effective as shown through our EIS experiments, as capacity loss with each cycle has drastically decreased. Cyclized PAN was found to be the most effective, possibly due to the cyclization of PAN increasing the mechanical effectiveness of the coating, while also increasing its ability to transfer Li ions. However, rate tests show the limitation of the cPAN coating, with a sudden limitation of the material to retain capacity at 10C. While this study highlights the benefits of these additives, SWCNT and PAN, the study ultimately shows the need for protection of this class of large volume expanding alloy anodes for lithium-ion systems. Alloy materials continue to be plaqued with mechanical stability issues and excessive growth of

SEI that limits its survivability. This suggests the future of stabilizing alloy anodes may be related to research on coatings and additives into the system.

7.6 References

1. *Electrochemical Energy Storage Technical Team Roadmap*; September 2017, 2017.

2. Sharma, R. A.; Seefurth, R. N., Thermodynamic Properties of the Lithium-Silicon System. *J. Electrochem. Soc.* **1976**, *123* (12), 1763-1768.

3. Wilson, A. M.; Reimers, J. N.; Fuller, E. W.; Dahn, J. R., Lithium insertion in pyrolyzed siloxane polymers. *Solid State Ionics* **1994**, *74* (3), 249-254.

4. Wilson, A. M.; Way, B. M.; Dahn, J. R.; Buuren, T. v., Nanodispersed silicon in pregraphitic carbons. *Journal of Applied Physics* **1995**, *77* (6), 2363-2369.

5. Wang, C. S.; Wu, G. T.; Zhang, X. B.; Qi, Z. F.; Li, W. Z., Lithium Insertion in Carbon-Silicon Composite Materials Produced by Mechanical Milling. *J. Electrochem. Soc.* **1998**, *145* (8), 2751-2758.

6. Ying, H.; Han, W.-Q., Metallic Sn-Based Anode Materials: Application in High-Performance Lithium-Ion and Sodium-Ion Batteries. *Advanced Science* **2017**, *4* (11), 1700298.

7. Xin, F.; Whittingham, M. S., Challenges and Development of Tin-Based Anode with High Volumetric Capacity for Li-Ion Batteries. *Electrochemical Energy Reviews* **2020**.

8. Beaulieu, L. Y.; Eberman, K. W.; Turner, R. L.; Krause, L. J.; Dahn, J. R., Colossal Reversible Volume Changes in Lithium Alloys. *Electrochemical and Solid-State Letters* **2001**, *4* (9), A137.

9. Park, S.-H.; King, P. J.; Tian, R.; Boland, C. S.; Coelho, J.; Zhang, C.; McBean, P.; McEvoy, N.; Kremer, M. P.; Daly, D.; Coleman, J. N.; Nicolosi, V., High areal capacity battery electrodes enabled by segregated nanotube networks. *Nature Energy* **2019**, *4* (7), 560-567.

10. Allcorn, E.; Kim, S.-O.; Manthiram, A., Thermal stability of active/inactive nanocomposite anodes based on Cu2Sb in lithium-ion batteries. *J. Power Sources* **2015**, *299*, 501-508.

11. Leibowitz, J.; Allcorn, E.; Manthiram, A., SnSb-TiC-C nanocomposite alloy anodes for lithium-ion batteries. *J. Power Sources* **2015**, *279*, 549-554.

12. Allcorn, E.; Manthiram, A., High-rate, high-density FeSb–TiC–C nanocomposite anodes for lithium-ion batteries. *J. Mater. Chem. A* **2015**, *3* (7), 3891-3900.

13. Yoon, S.; Manthiram, A., Sb-MOx-C (M = Al, Ti, or Mo) Nanocomposite Anodes for Lithium-Ion Batteries. *Chem. Mater.* **2009**, *21* (16), 3898-3904.

14. Allcorn, E.; Manthiram, A., NiSb–Al2O3–C Nanocomposite Anodes with Long Cycle Life for Li-Ion Batteries. *The Journal of Physical Chemistry C* **2014**, *118* (2), 811-822.

15. Allcorn, E.; Manthiram, A., FeSb2–Al2O3–C Nanocomposite Anodes for Lithium-Ion Batteries. *ACS Appl Mater Interfaces* **2014**, *6* (14), 10886-10891.

16. Li, N.; Yi, Z.; Lin, N.; Qian, Y., An Al2O3 coating layer on mesoporous Si nanospheres for stable solid electrolyte interphase and high-rate capacity for lithium ion batteries. *Nanoscale* **2019**, *11* (36), 16781-16787.

17. Wang, F.; Chen, G.; Zhang, N.; Liu, X.; Ma, R., Engineering of carbon and other protective coating layers for stabilizing silicon anode materials. *Carbon Energy* **2019**, *1* (2), 219-245.

18. Piper, D. M.; Yersak, T. A.; Son, S.-B.; Kim, S. C.; Kang, C. S.; Oh, K. H.; Ban, C.; Dillon, A. C.; Lee, S.-H., Conformal Coatings of Cyclized-PAN for Mechanically Resilient Si nano-Composite Anodes. *Advanced Energy Materials* **2013**, *3* (6), 697-702.

19. Fang, S.; Shen, L.; Nie, P.; Xu, G.; Wang, J.; Zhang, X., High performance threedimensional Ge/cyclized-polyacrylonitrile thin film anodes prepared by RF magnetron sputtering for lithium ion batteries. *Journal of Materials Science* **2014**, *49* (5), 2279-2285.

20. Shen, L.; Shen, L.; Wang, Z.; Chen, L., In Situ Thermally Cross-linked Polyacrylonitrile as Binder for High-Performance Silicon as Lithium Ion Battery Anode. *ChemSusChem* **2014**, *7* (7), 1951-1956.

21. Xie, M.; Piper, D. M.; Tian, M.; Clancey, J.; George, S. M.; Lee, S.-H.; Zhou, Y., Doped Si nanoparticles with conformal carbon coating and cyclized-polyacrylonitrile network as high-capacity and high-rate lithium-ion battery anodes. *Nanotechnology* **2015**, *26* (36), 365401.

22. Sun, Y.; Dong, H.; Xu, Y.; Zhang, Y.; Zhao, C.; Wang, D.; Liu, Z.; Liu, D., Incorporating cyclized-Polyacrylonitrile with Li4Ti5O12 Nanosheet for High Performance Lithium Ion Battery Anode Material. *Electrochim. Acta* **2017**, *246*, 106-114.

23. Lang, J.; Song, J.; Qi, L.; Luo, Y.; Luo, X.; Wu, H., Uniform Lithium Deposition Induced by Polyacrylonitrile Submicron Fiber Array for Stable Lithium Metal Anode. *ACS Appl Mater Interfaces* **2017**, *9* (12), 10360-10365.

24. Nguyen, Q. H.; Kim, I. T.; Hur, J., Core-shell Si@c-PAN particles deposited on graphite as promising anode for lithium-ion batteries. *Electrochim. Acta* **2019**, *297*, 355-364.

25. Chen, P.; Huang, W.; Liu, H.; Cao, Z.; Yu, Y.; Liu, Y.; Shan, Z., Enhanced cyclability of silicon anode via synergy effect of polyimide binder and conductive polyacrylonitrile. *Journal of Materials Science* **2019**, *54* (12), 8941-8954.

26. Zhang, W.; Sun, M.; Yin, J.; Abou-Hamad, E.; Schwingenschlögl, U.; Costa, P. M. F. J.; Alshareef, H. N., Cyclized polyacrylonitrile anode for alkali metal ion batteries. *Angewandte Chemie International Edition n/a* (n/a).

27. Sahalie, N. A.; Wondimkun, Z. T.; Su, W.-N.; Weret, M. A.; Fenta, F. W.; Berhe, G. B.; Huang, C.-J.; Hsu, Y.-C.; Hwang, B. J., Multifunctional Properties of Al2O3/Polyacrylonitrile Composite Coating on Cu to Suppress Dendritic Growth in Anode-Free Li-Metal Battery. *ACS Applied Energy Materials* **2020**, *3* (8), 7666-7679.

28. Dunlap, N. A.; Kim, J.; Oh, K. H.; Lee, S.-H., Slurry-Coated Sheet-Style Sn-PAN Anodes for All-Solid-State Li-Ion Batteries. *J. Electrochem. Soc.* **2019**, *166* (6), A915-A922.

29. Schulze, M. C. Thesis: Using antimony as a model anode to study the chemical and mechanical stability of electrodes in Li-ion and next generation batteries. Colorado State University, 2019.

30. Schulze, M. C.; Schulze, R. K.; Prieto, Amy L., Electrodeposited thin-film CuxSb anodes for Li-ion batteries: enhancement of cycle life via tuning of film composition and engineering of the film-substrate interface. *J. Mater. Chem. A* **2018**, *6* (26), 12708-12717.

31. Ma, J.; Prieto, A. L., Understanding The Electrodeposition of Pure Phase Crystalline SnSb from Deep Eutectic Ethaline Solution and Its Application as a Lithium-Ion Anode. *J. Electrochem. Soc.* In submission.

32. Magasinski, A.; Zdyrko, B.; Kovalenko, I.; Hertzberg, B.; Burtovyy, R.; Huebner, C. F.; Fuller, T. F.; Luzinov, I.; Yushin, G., Toward Efficient Binders for Li-Ion Battery Si-Based Anodes: Polyacrylic Acid. *ACS Appl Mater Interfaces* **2010**, *2* (11), 3004-3010.

33. Mazouzi, D.; Karkar, Z.; Reale Hernandez, C.; Jimenez Manero, P.; Guyomard, D.; Roué, L.; Lestriez, B., Critical roles of binders and formulation at multiscales of silicon-based composite electrodes. *J. Power Sources* **2015**, *280*, 533-549.

34. Xu, J.; Zhang, Q.; Cheng, Y.-T., High Capacity Silicon Electrodes with Nafion as Binders for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2015**, *163* (3), A401-A405.

CHAPTER 8 – ELECTROCHEMICAL SYNTHESIS OF Mg₃PO₄ – AN ATTEMPT TO SYNTHESIZE IONIC CONDUCTORS THROUGH ELECTROCHEMICAL CORROSION⁸

8.1 Overview

The use of electrochemical corrosion can help identify promising ionic conductors. Here, we look to better control the corrosion of $Mg_3(PO_4)_2$ coating on Mg metal. Through controlling different experimental parameters, we identify the use of electrochemistry during the corrosion process leads to more control over the desired composition and morphology of the product.

8.2 Introduction

The search for new ionic conductors and methods of producing ionically conductive coating is desirable with the increasing interest in applications such as fuel cells, batteries, sensors, and other similar electrochemical systems. Due to uncontrollable interactions altering the surface of the electrode when under operation in electrochemical systems, ionically conductive coatings are desired to protect the active material surface from undesirable interface interactions. For rechargeable battery technologies, coatings are utilized as protection for electrode surfaces from directly contacting the electrolyte and electrolyte decomposition products during continuous electrochemical cycling. The solid electrolyte interface (SEI), an interface formed from interaction of an electrode with the decomposing electrolyte, has been found to alter the electrode surface and can inhibit ion mobility when not controlled.¹⁻³ More specifically, SEI has been found to inhibit ion mobility and metal re-plating of multivalent metals in common electrochemistry solvents.⁴⁻⁸ Due to this fact, Mg metal plating and stripping does not utilize carbonate solvents typically found in Lithium-ion technologies and instead currently relies on highly corrosive and oxidation sensitive electrolytes that inhibit SEI growth.⁹⁻¹⁰ Ideally, coatings

⁸ This chapter is written by Jeffrey Ma with the guidance from Amy L. Prieto. J.M. would like to thank Jacob Schneider (Prieto Group, Colorado State University) for their suggestions in writing this chapter.

will protect the multivalent metal from the unwanted SEI formation while allowing sufficient ion mobility and even re-plating of the active material underneath the coating.

Currently, there is no systematic method regularly utilized for quickly identifying ionic conductors through experimental means, while some computational means exist, these are limited in the scope of materials. Ideally, the experimental method to search for ionic conductors should not only result in the production of the ionic material, but also allow for tunability and control of the way ionic conductors are formed. Electrochemical corrosion allows for control of current passed, which results in control over the thickness of coating formed. Tests performed in small solutions in a laboratory can easily be scaled up to larger production though the utilization of this synthetic method.

In this study, we will be exploring the electrochemical corrosion of Mg₃(PO₄)₂ onto Mg surface. Phosphate coatings have been found to be successful as ionically conductive coatings in similar systems.¹¹⁻¹⁴ Only few literature reports have been produced on the production of Mg₃(PO₄)₂, with most Mg₃(PO₄)₂ work published in the corrosion field as a corrosion resistant coating.¹⁵⁻¹⁹ Mg metal is explored first in this study as it is sufficiently stable in a wide variety of solvents, including aqueous solutions. Na and Li metals are found to be too difficult to stabilize for our desired corrosion of a coating, as many of the desired salts and solvents were tested and found to be either insoluble or outside of the window of stability for controlled corrosion. Mg will allow for the initial exploration of electrochemical corrosion for an evenly coated surface. Different methods of corrosion and electrochemical sequences will be explored to identify the effect of each parameter on the resulting surface corrosion product.

8.3 Experimental Methods

Spontaneous corrosion experiments were performed by submerging Mg ribbon into 1 M phosphate aqueous solutions. The phosphate precursors primarily used in these experiments
includes K₃PO₄ (reagent grade, \geq 98%, Sigma Aldrich), and Na₃PO₄ (96%,Sigma Aldrich). NH₄H₂PO₄ (ACS reagent, \geq 98%, Sigma Aldrich), (NH₄)₂HPO₄ (ACS reagent, \geq 98%, Sigma Aldrich), LiH₂PO₄ (monobasic, 99%, Sigma Aldrich), Li₃PO₄ (Sigma Aldrich), H₃PO₄ (85% Certified ACS, Fisher), K₂HPO₄ (ACS reagent, \geq 98%, Sigma Aldrich), KH₂PO₄ (ACS reagent, \geq 99.0%, Sigma Aldrich), Na₂HPO₄ (ACS reagent, \geq 99.0%, Sigma Aldrich), NaH₂PO₄ (ACS reagent, \geq 99.0%, Sigma Aldrich), Na₂HPO₄ (ACS reagent, \geq 99.0%, Sigma Aldrich), NaH₂PO₄ (ACS reagent, \geq 98%, Sigma Aldrich), Tetrahydrofuran (reagent 99%, Sigma Aldrich), Diethyl carbonate (99%, Sigma Aldrich), Propylene Carbonate (anhydrous, 99.7%, Sigma Aldrich), N,N-Dimethylformamide (99.8%, Sigma Aldrich), Acetonitrile (ACS reagent, \geq 99.5%, Sigma Aldrich), Hexane (anhydrous, 95%, Sigma Aldrich), and N-methyl-2-pyrrolidone (ACS reagent, \geq 99.0%, Sigma Aldrich) were also used in this set of experiments. Stirring was introduced by the addition of a Teflon based magnetic stir bar.

The electrochemical corrosion performed was set up in a three- electrode cell utilizing the Gamry 3000 potentiostat. Mg ribbon was utilized as the working electrode the coating was corroded onto. Prior to the use of the Mg ribbon, a scouring pad was used to remove the oxide layer present on the surface of the electrode. A Kapton film was applied to the backside of the metal to allow for corrosion to only occur on one side. A saturated calomel electrode was used as the reference electrode, and stainless-steel mesh (PO# AC-75973470, Elmhurst) as the counter electrode. In this study, some corrosion occurred using a process we call applied voltage entry. Applied voltage entry is a method of which potential is applied to the 3-electrode cell as it is submerged into the solution. This method is used to ensure better control of Mg corrosion through electrochemical means to dictate the products product and not allow any spontaneous corrosion products to form on the electrode surface prior to applying an electrochemical potential on the system.

The crystallinity of the corroded products were identified using a Bruker D8 Discover DaVinci (Cu K α radiation, λ = 1.54184 Å) X-ray diffractometer. The morphology found present on

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the surface of the electrodes and its atomic compositions were examined using a scanning electron microscope (SEM; JOEL JSM-6500F) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (Oxford Instrument X-Max). The atomic ratios are identified by using the Aztec software (Oxford Instrument) that fits the EDS spectra obtained.

8.4 Results and Discussion

8.4.1 Initial survey of the solubility of different salts

Salt (bottom)/Solvent (right)	THF	DEC	PC	DMF	ACN	Hexane	Methanol	NMP	Water
Ammonium dihydrogen phosphate	N	N	N	N	N	-	-	N	Y
Ammonium hydrogen phosphate	N	N	N	N	N	N	Ν	-	Y
Lithium dihydrogen phosphate	N	N	N	N	N	-	-	-	N
Lithium phosphate	N	N	N	N	N	N	Ν	-	N
Phosphoric acid	Y	-	-	-	-	-	-	-	Y
Potassium phosphate, dibasic	N	N	N	N	N	-	-	-	Y
Potassium phosphate, monobasic	N	N	N	N	N	-	-	-	Y
Potassium phosphate, tribasic	N	N	N	N	N	-	-	-	Y
Sodium phosphate monobasic monohydrate	N	N	N	N	N	-	-	-	Y
Sodium phosphate, dibasic	N	N	N	N	N	-	-	-	Y
Sodium phosphate, tribasic	N	N	N	N	N	-	-	-	Y

Table 1: Solubility of different salts in selected solvents.

In search of solutions to use for the electrochemical corrosion of ionic conductors, the solubility of salts remains a hindrance to the solutions available for the exploratory search. Table 1 identifies the solubility of a mixture of various phosphate salts and solvents. The solvents were chosen due to the possibility that a solution can be made that allows for controlled corrosion of a metal surface. Due to incompatibility of lithium and sodium salt in non-aqueous solutions, the corrosion of Na or Li metal is difficult to achieve. The successful corrosion of very negative potential metals, such as sodium and lithium, requires a combination of a dissolved salt in solvent

with a large enough electrochemical stability window in the range of Na and Li stability that will remain unreactive or low in reactivity with the submergence of the metal. Solvents, like water, that fall outside of the stability window with Li and Na results in immediate reaction with the metal and the dissolution of the metal into the solution. With the lack of soluble salt and solvents available from the initial screening, Mg metal is focused on moving forward, as it is relatively stable in water for the initial screening using electrochemical corrosion.

8.4.2 Effect of precursor solution composition on the resulting Mg phosphate surface morphology

Products of Mg corrosion and the morphology of the resulting film are identified to be highly affected based on initial precursor used. Phosphate precursors containing hydrogen (mono or di hydrogen) were found to unfavorably affect the surface morphology. When current is applied and the Mg metal is submerged into the solution, bubbles are rapidly produced on the surface of the Mg metal and visible macroscopically. Formation of pitting or a porous structured surface is macroscopically visible after being taken out of the solution, as identified in the SEM images presented in figure 8.1, suggesting possible hydrogen evolution during Mg corrosion. This hydrogen or gas production is highly unfavorable, as the hydrogen bubbles will cause uneven corrosion and the subsequent production of the desired coating, with the pockets of gas formed on the surface of the metal possibly inhibiting areas of unreacted Mg from reacting with the bulk of the solution. In order to resist gas buildup on the surface during corrosion, phosphoric acid and hydrogen containing precursors were not used in later experiments.

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Figure 8.1: SEM images of different areas of an Mg metal surface after being submerged in 1 M $NH_4H_2PO_4$ in water overnight. Gas formation occurred throughout the corrosion process, resulting in the uneven corrosion on the surface presented.

Submerging Mg in water typically can cause a slow reaction with water to form Mg(OH)₂ or MgO over time. In order to mitigate hydroxide dissolution and MgO on the surface, adding HCI was planned. However, HCI leads to destruction of film due to an exothermic reaction with MgCI and H₂ formation. No instrumental data was obtained for this film, as the film broke off and eventually dissolved in the solution. The pH of the solution was also monitored and found to be more basic after the reaction, suggesting the hydroxide formation in the solution.

8.4.3 How the applied electrochemical sequence and convection changes the Mg phosphate product and morphology

Ideally, the corrosion synthesis would result in the formation of the desired product, Mg₃(PO₄)₂ without the presence of the precursor cation pair on the corroded surface. Throughout the experiments, we have discovered that intermediate corrosion products can be isolated with the formation of mixed-Mg/A (A=Na, K) phosphates products depending on specific methods utilized during the corrosion synthesis. One example of this mixed- ion product formation is through passive corrosion, where the Mg metal is submerged into the solution and no potential is

applied. When no current is passed, the spontaneous corrosion will result in the partial reaction of the dissolved salt precursor onto the Mg metal surface. As shown in figure 8.2, after the spontaneous corrosion of Mg metal in K₃PO₄, the resulting crystalline product MgKPO₄ is found. However, SEM images suggest the surface of the electrode is unevenly reacted with partial corrosion across the surface and cracks present throughout the corroded film, suggesting a poorly controlled reaction of the surface through this spontaneous reaction method.



Figure 8.2: a) XRD pattern and b) SEM image of Mg corroded for 24 hours in 1M K_3PO_4 aqueous solution.

Initial studies where an electrochemical potential is applied to the Mg metal upon introduction into the precursor solution also showed similar crystalline mixed ion products. Presented in figure 8.3a is the XRD product of the Mg surface in a K₃PO₄ solution after a potential

of 5V vs SCE was applied for 7900s. The XRD presents a similar formation of crystalline product in the form of KMgPO₄. The surface of the corroded Mg however, demonstrates that using applied voltage entry reduced major cracks seen on the surface. The surface morphology of the applied voltage entry product resulted in smaller, more homogenous and similar sized facets on the surface when compared to the spontaneous corrosion. This suggests that applied voltage entry has an effect in controlling the even growth and electrochemical corrosion and can allow for more control than unregulated corrosion. While more control of the crystalline growth on the Mg surface is obtained for the applied voltage entry corrosion, the surface still remains uneven with areas of more crystalline growth than other areas, as seen in the SEM image in figure 8.3b.



Figure 8.3: a) XRD pattern and b) SEM image of the surface of Mg metal after applied voltage entry corrosion at 5 V vs SCE for 7900s.

The potential at which the applied voltage entry occurs has also been identified to influence the resulting products. The difference in crystalline products based on XRD for a Mg metal that had an applied voltage entry of 5 V vs SCE and another Mg metal with 0 V vs SCE potential applied when submerged into Na₃PO₄ solution is presented in figure 8.4a. The crystalline

pattern, based on the XRD, indicates a more crystalline product, specifically observed with the more intense peaks at 32.5° and 33.5° 2 Θ for the sample with potential applied at 0 V vs SCE, signifying more crystalline NaMgPO₄ product. EDS (figure 8.4b) further verifies more of the NaMgPO₄ was produced on the Mg surface at 0 V vs SCE with the presence of lower O:P content (1 : 4.4 O:P) that suggests less MgO formation and a closer atomic composition to -PO₄ present at this potential.



Figure 8.4: a) XRD and b) EDS comparing applied voltage entry of Mg into 1 M Na_3PO_4 aqueous solution at 5 V vs SCE or 0 V vs SCE for 7200s.

Stirring during the corrosion process was introduced and was found to have a greater effect on not only the crystalline product produced, but also the even corrosion on the Mg surface. Presented on figure 8.5 is the spontaneous corrosion of two Mg metal substrates submerged into Na₃PO₄ solution for 15 hours, one left static in the solution while the other with convection in the solution. Comparing the crystalline products present on the surface of the two metals, the unstirred metal resulted in more crystalline NaMgPO₄ with the formation of different MgPO₄ products. The stirred metal resulted in the reduced presence of the mixed ion phosphate, NaMgPO₄, and an increase in crystalline MgPO₄ products present. This suggest that stirring is more favorable when targeting the fully reacted phosphate product (Mg₃(PO₄)₂). Stirring during the corrosion also resulted in a more even, but less crystalline, growth of the phosphate products on the surface of the Mg metal, based on SEM. EDS further verifies a more -PO₄ surface and less MgO present based on the atomic composition present on the surface of the film for the stirred corrosion (1 : 3.8 P:O ratio).





Figure 8.5: a) XRD patterns and b) EDS comparing the corrosion of Mg in a 1M Na₃PO₄ aqueous solution that is unstirred and stirred during the corrosion process. SEM image of the surface of Mg corrosion c) unstirred and d) stirred during the process. Note that unstirred was at x150 magnification to show the uneven growth and not the x1000 magnification normally presented.

The applied voltage entry was also found to have a difference between an open cell reaction, where the oxidizing current passed on the Mg working electrode is exposed to air with the solution in a beaker, and a closed electrochemical cell reaction, where applied voltage entry of the Mg metal occurs in a solution that is capped. Figure 8.6 identifies the products of different closed cell applied voltage entry corrosion of Mg with time in a Na₃PO₄ solution where no stirring occurred. When comparing the product of the corrosion process across different times of applied potential, the crystalline product grows in intensity and becomes more crystalline with time. However, comparing this closed cell reaction with the open cell reaction that occurred in figure 8.4, where both applied voltage entry reactions occurred at 0 V vs SCE, we identified the product from the close cell process to be more crystalline and the reaction is driven more to completion with a higher intensity of crystalline Mg₃(PO₄)₂ formed.



Figure 8.6: XRD pattern comparing Mg applied voltage entry corrosion in a closed cell solution of 1 M Na_3PO_4 sequences at 0 V vs SCE at different corrosion times.

In order to increase the uniform formation of a crystalline and even coating of Mg₃(PO₄)₂ on the surface, applied voltage entry in a closed cell was done in conjunction with stirring. Previously, stirring was identified to help drive the reaction to completion with the formation of more crystalline Mg₃(PO₄)₂ and a more even surface. Figure 8.5 demonstrate that the addition of stirring resulted in higher crystallinity of Mg₃(PO₄)₂ formed. To further increase the evenness of the film, pulsed deposition sequence was applied instead of a constant potential sequence. Based on SEM images presented, constant potential continues to result in uneven growth of crystalline products on the surface, resulting in regions of micron sized crystalline growth while other areas contain nanometer sized products. Pulsed potential can decrease growth of specific nucleation sites by allowing a rest period to replenish the depleted ions at the surface of the electrode for a more even nucleation of the corroded film. The resulting film yielded a less crystalline product, based on XRD (figure 8.7), but a more even surface based on SEM.



Figure 8.7: XRD pattern and SEM images (a-f) comparing different Mg applied voltage entry corrosion in a closed cell solution of 1 M Na_3PO_4 sequences including 0 V vs SCE unstirred (a,b) and stirred (c,d) corrosions, and pulsing sequence of 0 V vs SCE for 15s, rest 1s for 480 cycles (e,f). Both pulse and constant corrosion experiments should have the same total time at which potential was applied to the working electrode.

Further tuning of the pulsing sequence resulted in better control over the film morphology and smaller facets found on the film surface. Through this, we have determined that morphology is affected greatly by the pulsing sequence employed for this system. Shown on figure 8.8, even coverage of surface throughout the film is found, and particle size of the crystallites has decreased. This suggests that even growth can be dictated by pulse and rest times.



Figure 8.8: XRD (top) and SEM images (bottom, a-d) of) comparing different Mg applied voltage entry corrosion in a closed cell solution of $1 \text{ M Na}_3\text{PO}_4$ pulsing sequences of 15s pulse, 1s rest for 480 cycles (a,b), and 1s pulse, 1s rest for 7200s (c,d). The pulse applied is 0 V vs SCE and pulsing sequences should have the same total time at which potential was applied to the working electrode.

8.5 Conclusion

In summary, we have investigated different parameters that impact the even electrochemical corrosion of Mg₃(PO4)₂ onto a Mg metal electrode surface. We have identified partially reacted products, in the form of a mixed-ion product, through corrosion without convection. The application of applied voltage entry, where an oxidative voltage is applied to the working electrode in a three-electrode setup as it is submerged into the solution and the circuit is completed, resulted in a more even and less cracked deposition of the coating. Further control of the corrosion occurred through using a combination of a closed electrochemical cell and a pulsing sequence, which lowered the amount of MgO present in the product and resulted in smaller, more even crystallites being formed across the surface of the corroded film. With the successful production of an even coating, future directions may include electrochemical testing of the $Mg_3(PO_4)_2$ film as an effective coating for uniform Mg stripping and re-plating. The conductivity of the Mg₃(PO₄)₂ can be further improved through the attempted synthesis and formation of MgPON. The doping of nitrogen into lithium analogue, Li₃PO₄, produced the solid conductor LiPON, which resulted in an enhancement of the material's ionic conductivity.²⁰⁻²¹ While only one report has been presented on the idea of MgPON, the synthesis of MgPON is not very well described and may require extensive focus prior to electrochemically testing the material.²²⁻²³

8.6 Reference

1. Peled, E.; Yamin, H., Solid Electrolyte Interphase (SEI) Electrodes. Part 1. The Kinetics of Lithium in LiAlCl4-SOCl2. *Israel Journal of Chemistry* **1979**, *18* (1-2), 131-135.

2. Peled, E.; Menkin, S., Review—SEI: Past, Present and Future. *J. Electrochem. Soc.* **2017**, *164* (7), A1703-A1719.

3. Börner, M.; Friesen, A.; Grützke, M.; Stenzel, Y. P.; Brunklaus, G.; Haetge, J.; Nowak, S.; Schappacher, F. M.; Winter, M., Correlation of aging and thermal stability of commercial 18650-type lithium ion batteries. *J. Power Sources* **2017**, *342*, 382-392.

4. Connor, J. H.; Reid, W. E.; Wood, G. B., Electrodeposition of Metals from Organic Solutions. *J. Electrochem. Soc.* **1957**, *104* (1), 38.

5. Gregory, T. D.; Hoffman, R. J.; Winterton, R. C., Nonaqueous Electrochemistry of Magnesium: Applications to Energy Storage. *J. Electrochem. Soc.* **1990**, *137* (3), 775-780.

6. Aurbach, D.; Weissman, I.; Gofer, Y.; Levi, E., Nonaqueous magnesium electrochemistry and its application in secondary batteries. *The Chemical Record* **2003**, *3* (1), 61-73.

7. Staniewicz, R. J., A Study of the Calcium-Thionyl Chloride Electrochemical System. *J. Electrochem. Soc.* **1980**, *127* (4), 782-789.

8. Aurbach, D.; Skaletsky, R.; Gofer, Y., The Electrochemical Behavior of Calcium Electrodes in a Few Organic Electrolytes. *J. Electrochem. Soc.* **1991**, *138* (12), 3536-3545.

9. Muldoon, J.; Bucur, C. B.; Gregory, T., Quest for Nonaqueous Multivalent Secondary Batteries: Magnesium and Beyond. *Chemical Reviews* **2014**, *114* (23), 11683-11720.

10. Mohtadi, R.; Mizuno, F., Magnesium batteries: Current state of the art, issues and future perspectives. *Beilstein Journal of Nanotechnology* **2014**, *5*, 1291-1311.

11. Huang, J.; Luo, J., A facile and generic method to improve cathode materials for lithiumion batteries via utilizing nanoscale surface amorphous films of self-regulating thickness. *Physical Chemistry Chemical Physics* **2014**, *16* (17), 7786-7798.

12. Hao, S.; Ma, Z.; Zhao, Y.; Kong, L.; He, H.; Shao, G.; Qin, X.; Gao, W., In Situ Li3PO4/PVA Solid Polymer Electrolyte Protective Layer Stabilizes the Lithium Metal Anode. *ACS Omega* **2020**, *5* (14), 8299-8304.

13. Lee, Y.; Lee, J.; Lee, K. Y.; Mun, J.; Lee, J. K.; Choi, W., Facile formation of a Li3PO4 coating layer during the synthesis of a lithium-rich layered oxide for high-capacity lithium-ion batteries. *J. Power Sources* **2016**, *315*, 284-293.

14. Chen, D.; Zheng, F.; Li, L.; Chen, M.; Zhong, X.; Li, W.; Lu, L., Effect of Li3PO4 coating of layered lithium-rich oxide on electrochemical performance. *J. Power Sources* **2017**, *341*, 147-155.

15. Zhao, H.; Cai, S.; Ding, Z.; Zhang, M.; Li, Y.; Xu, G., A simple method for the preparation of magnesium phosphate conversion coatings on a AZ31 magnesium alloy with improved corrosion resistance. *RSC Adv.* **2015**, *5* (31), 24586-24590.

16. Jayaraj, J.; Amruth Raj, S.; Srinivasan, A.; Ananthakumar, S.; Pillai, U. T. S.; Dhaipule, N. G. K.; Mudali, U. K., Composite magnesium phosphate coatings for improved corrosion resistance of magnesium AZ31 alloy. *Corrosion Science* **2016**, *113*, 104-115.

17. Quintana-Camacho, H., Investigation of the corrosion behavior of phosphate coated magnesium in a Kokubo Solution. *Int. J. Electrochem. Sci.* **2018**, *13*, 6072-6082.

18. Su, J.; Tsuruoka, T.; Tsujita, T.; Nishitani, Y.; Nakura, K.; Terabe, K., Atomic Layer Deposition of a Magnesium Phosphate Solid Electrolyte. *Chem. Mater.* **2019**, *31* (15), 5566-5575.

19. Tsuruoka, T.; Tsujita, T.; Su, J.; Nishitani, Y.; Hamamura, T.; Inatomi, Y.; Nakura, K.; Terabe, K., Fabrication of a magnesium-ion-conducting magnesium phosphate electrolyte film using atomic layer deposition. *Japanese Journal of Applied Physics* **2020**, *59* (SI), SIIG08.

20. Suzuki, N.; Shirai, S.; Takahashi, N.; Inaba, T.; Shiga, T., A lithium phosphorous oxynitride (LiPON) film sputtered from unsintered Li3PO4 powder target. *Solid State Ionics* **2011**, *191* (1), 49-54.

21. Le Van-Jodin, L.; Claudel, A.; Secouard, C.; Sabary, F.; Barnes, J.-P.; Martin, S., Role of the chemical composition and structure on the electrical properties of a solid state electrolyte: Case of a highly conductive LiPON. *Electrochim. Acta* **2018**, *259*, 742-751.

22. Magnesium Phosphorus Oxynitride with High Mg2+ Ionic Conductivity as a Novel Thinfilm Magnesium Electrolyte. *ECS Meeting Abstracts* **2016**.

23. Satoshi Shibata, Y. N., Takuji Tsujita Solid electrolyte containing oxynitride, and secondary battery including the solid electrolyte. US Patent US10074872B2. 2016.

CHAPTER 9 – ROOM TEMPERATURE STRIPPING AND PLATING OF CALCIUM METAL IN CARBONATE SOLVENT THROUGH A CA-SN COATING⁹

9.1 Overview

Studies utilizing Calcium metal as an anode are limited due to the lack of compatibility between the Calcium surface with electrolyte systems resulting in limited Calcium plating. Here, the design of different Ca-alloy coatings through corrosion is investigated as an effective way to allow for Calcium plating and to protect the calcium surface from the detrimental electrolyte surface formation. Through different electrochemical experiments, we have identified the coating is effective in forming a barrier that enables more even stripping and re-plating.

9.2 Introduction

Energy storage will be crucial in the upcoming decades as our society focuses on electrifying our grid while lessening our reliance on oil to reduce carbon emissions that affect the climate and environment. Currently, lithium-ion battery technology leads the way in energy storage, as its technology continues to enable portable electronic devices. The search for continuous advancements of energy storage technologies to higher energy densities have led to research on multivalent battery technologies such as Ca, Mg, or Al. These multivalent ion technologies have risen as promising alternatives as they are more abundant, would greatly reduce costs, and lessen the current over-demand of lithium-ion batteries for non-portable storage technologies. Ideally, multivalent ions should double the capacities seen in lithium technology as it contains at least twice the ions. Current research on multivalent ion systems has greatly focused on Mg, although Ca should ideally be the better divalent candidate. Ca is a more abundant element in the earth's crust (5th most abundant vs 7th most abundant for Mg), provides a more

⁹ This chapter is written by Jeffrey Ma with the guidance from Amy L. Prieto. J.M. would like to thank Kelly Nieto (Prieto Group, Colorado State University) for their suggestions in writing this chapter.

negative reductive potential (- 2.87V vs standard hydrogen electrode (SHE); Mg is -2.37V vs SHE), and should ideally be easier to move Ca²⁺ ions in liquid electrolyte due to lower polarizability and attraction. However, like other multivalent systems mentioned, Ca is plagued with problems related to the growth of passivating layers during cycling that inhibits its ability to further plate. Due to this challenge, not much research has been done that enables the stripping and plating of Ca metal.

Initial studies on stripping and plating of Ca metal can be dated back to work performed in 1980 at GTE Laboratories, where researchers attempted to study the electrochemistry of Calcium metal in a SOCI₂ electrolyte.¹ Through this study, a CaCI₂ passivating layer was identified to form, which limited the mobility of Ca ions through this interface on the calcium surface and inhibited the plating process. In 1991, Aurbach and coworkers attempted to study Ca metal plating and stripping in a suite of commonly found salts and organic electrolytes that included $Ca(CIO_4)_2$ and Ca(BF₄)₂ in acetonitrile, tetrahydrofuran, and propylene carbonate (PC).² Again, the irreversibility of Ca metal plating was identified through electrochemical experiments and believed to be related to the formation of an inhibiting passivating layer. Progress in calcium plating and stripping does not occur for more than 25 years, with Ponrouch and coworkers first reporting the successfully plating and stripping Calcium in an electrolyte heated at an elevated temperature of 100° C through the use of an electrolyte formulation containing $Ca(BF_4)_2$ in an ethylene carbonate (EC)/ PC solvent.³ In 2018, the first room temperature plating and stripping of Calcium was reported, through the utilization of a Ca(BH₄)₂ in THF electrolyte.⁴ While this was a big accomplishment towards the practical use of Calcium metal anodes, the electrolyte does not have an electrochemical window that allows for the use of calcium metal with a potential high voltage cathode. Recently, the use of a Calcium electrolyte salt, Ca(B(Ohfip)₄)₂, was reported by two groups that enabled access to a large stability window of >4 V vs Ca/Ca⁺ and allowed Calcium stripping and plating at room temperature.⁵⁻⁶ While these groups have greatly advanced the field

by enabling room temperature rechargeable calcium metal batteries, calcium has yet to be utilized in common carbonate solvents and calcium salt analogues of formulations found in lithium-ion technology. The formulation of these electrolytes also opens up new questions related to Calcium metal during re-plating. Mg and Ca metals were favorable as anodes for these multivalent batteries due to the original belief that no dendritic growth occurs during the re-plating of these metals. However, recent research on Mg has identified the limits to this belief with the formation of Mg dendrites at high enough currents.⁷⁻⁸ This leaves questions about dendritic growth of Ca during replating and begins the search to avoid the dendritic re-plating of Calcium.

Recently, work in exploring alloy anodes for Ca-ion batteries has been reported.⁹ The experiment was successful in electrochemically alloying and dealloying Sn with Ca for over 1000 cycles before falling below 80% capacity retention in a calcium ion battery consisting of an electrolyte made of $Ca(PF_6)_2$ in carbonate solvents (EC, PC, dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC)). This suggests the passivating layer formed between Ca-Sn alloy and commonly found hexafluorophosphate salt with carbonate solvents is stable and does not form the same passivating layer that prevents Ca ion mobility. In recent years, other researchers focused on Li and Na metal technologies suggested the formation of a thin layer of alloy on metal surfaces can help protect the metal from interaction with electrolyte, while enabling even re-plating and preventing dendritic growth.¹⁰⁻¹³ This alloy coating/artificial solid electrolyte interface (SEI) can be beneficial, as it combines the fast ion conduction alloys possess while enabling a lower barrier re-plating process with the source of ions from the bulk metal underneath. Due to these previous studies, we believe the corrosion of a Ca-Sn surface on Ca metal will enable successful stripping and plating of Ca metal at room temperature in a carbonate solvent previously thought unable to be used. The success of this simple coating for room temperature stripping and plating enables the use of commonly used salts and solvents currently produced for the lithium-ion battery technology, allowing for ease in transferring technology. In this chapter, we will discuss

preliminary work performed on the Ca-Sn formed. We have identified initial data that suggests some benefits of the coating, although more experiments are required to be conclusive.

9.3 Experimental Methods

Ca metal (Alfa Aesar) chunks were flattened to < 1 µm thick metal of about ½" diameter in between two flat pieces of stainless steel using a hammer. The surface cleaned Ca metal is then submerged into 150 mM SnCl₂ (Sigma-Aldrich, anhydrous) or InCl₃ (Sigma-Aldrich, anhydrous) in THF for a specific amount of time for the desired thickness of Ca-M (M=Sn, In) coating. The surface of the Ca metal is found to turn from a shiny metallic surface to a gray surface once the metal submerges into the solution and the formation of the coating occurs.

0.8 M Ca(PF₆)₂ in propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC) (2:2:3 by volume) electrolyte was utilized for the experiments discussed in 9.4.1 and 9.4.2. Ca(PF₆)₂ was synthesized by slowly adding 327mg (1.0 mmol) NOPF₆ in 5 mL acetonitrile solution into a Ca metal (60 mg, 2.5 mmol, excess) in 5mL acetonitrile solution under an N₂ environment. The solution was stirred for 4 days. After 4 days, the solution was filtered in N₂ environment, and vacuum dried to remove the acetonitrile solvent by using a N₂ Schlenk line. Leaving it under vacuum by using the Schlenk line, the crystal Ca(PF₆)₂ salt was brought into an Ar environment to formulate the electrolyte.

0.25 M Ca[B(hfip)₄]₂ (CaBhfip) in dimethoxyethane (DME) was utilized for experiments discussed in 9.4.3. CaBhfip was synthesized by dissolving Ca(BH₄)₂ \cdot 2THF (3.21g, 15.0 mmol) in 60 mL DME. 20.50g (12.84 mL, 122 mmol) hexafluoro-2-propanol was slowly added into the previous solution. The mixture was then refluxed using an Ar Schlenk line at 90° C for 4 hours. The solution was then cooled to 40° C and left under vacuum overnight. The powder was then further heated at 60° C for 24 hours. The product was then sent into an Ar environment to formulate the desired electrolyte.

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The corroded Ca metals are then assembled into two electrode cells with a glass separator (Whatman) and desired electrolyte in between, in a coin cell configuration. The symmetric cells are tested galvanostatically by stripping and plating, with respect to the working electrode every 15 minutes. Cyclic voltammetry experiments were performed at 50 mVs⁻¹ scan rate.

9.4 Results and Discussion

9.4.1 Identifying the effect of coating thickness on its effectiveness

Initial experiments were performed to identify the thickness of the Ca-Sn required for effective protection of the Ca metal. Previous corrosion studies on Li and Na metals reported different corrosion times, resulting in an unclear relation between thickness and times required for the protection of the alkali metal. Presented in figure 9.1 is the plating and stripping of different Ca symmetric cells, including different corrosion times of the Ca-Sn coating formed and also a comparison of Ca-Sn coating to a Ca-In coating. The corrosion of an In alloy was investigated, as In was found to be the best performing alloy surface in a previous Li metal study.¹⁰ When comparing Ca-Sn and Ca-In coatings corroded for 10s, a higher impedance was identified for the Ca-In cell with every successive stripping and plating through the increasing overpotential. While the Ca-In symmetric cell showed instability and the buildup of the impedance, the Ca-Sn is identified to have relatively stable stripping and plating. Comparing the Ca-Sn coating resulted from 30s, the coating was found effective in lowering the impedance of the stripping and plating event when compared to the coating formed from 10s corrosion. However, the impedance remains slightly higher than the pure Ca/Ca cell tested in the initial stripping and plating processes, which is expected from the inclusion of a coating and the resulting extra interface present in the symmetric cells.

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Figure 9.1: Stripping and plating of different Ca symmetric cells. The cells highlighted differed in coating applied, time applied, and whether both the working and counter has the coating. The cells were stripped and plated at 0.1 mAcm⁻¹ rate for 15 minutes prior to operating in the opposite current. The figure at the bottom focuses on the comparison of the stripping and plating of a Ca-Sn symmetric cell and compares it to the Ca/Ca symmetric cell.

9.4.2 Cyclic voltammetry of Ca-Sn and Ca metal symmetric cells

While the preliminary studies have shown the increase in impedance of the symmetric stripping and plating of the cells containing the Ca-Sn coating, cyclic voltammogram was able to identify some benefits of the coating in protecting the Ca metal's ability to re-plate. Figures 9.2a and 9.2b are figures identifying the difference in the way cyclic voltammogram of a Ca/Ca cell occurs when compared to Ca-Sn/Ca-Sn symmetric cell. The CVs identify that the Ca-Sn cell was able to reach equilibrium after 8 cycles, while the Ca cell took 11 cycles to reach some equilibrium. When comparing the symmetric cells at equilibrium, figure 9.2c identifies the current at which stripping and plating occurs for the respective cells. The stripping and plating of both the Ca-Sn and Ca symmetric cells were found to occur at near 2 V and -2 V vs Ca/Ca⁺, respectively, and the high impedance is believed to possibly be related to the operation of the cells and electrolyte at room temperature. Based on the CV, the Ca-Sn cell possesses a more even coating with the stripping current of 0.7 A and plating current of -0.76 A, while the symmetric Ca/Ca cell without the coating had lower re-plating current of -0.51 A when compared to the stripping current of 0.6 A. Previous literature has already suggested the difficulties of Ca metal re-plating due to the formation of $Ca(OH)_2$, $CaCO_3$ and calcium alkoxides that result in a passivating layer that inhibits Ca ion mobility, and the cyclic voltammetry of the coating presented here suggests the ability of the coating to resist the re-plating problem.^{4, 14}



Figure 9.2: Cyclic voltammogram of a) Ca-Sn/Ca-Sn symmetric cells and how it compares to b) Ca/Ca symmetric cells. Cyclic voltammogram cycles occurred until equilibrium is reached and no drastic difference in current and stripping and plating peak is found. In order to compare the cells after it reaches equilibrium, c) was used to compare and identify the currents at which the stripping and plating was occurring.

The long term stripping and plating of Ca/Ca symmetric cell, Ca-Sn/Ca-Sn symmetric cell, and Ca/Ca-Sn asymmetric cell are presented in figure 9.3. The Ca/Ca symmetric cell was found to have a successive increase in impedance, with the increasing polarizability between stripping and plating potential over time and is experimentally stopped earlier than the cells containing the Ca metals with Ca-Sn cells. The Ca-Sn cells were successful in stripping and plating at times below the stripping and plating potential of ±2 V vs Ca/Ca⁺, but eventually resulted in greater than ±2 V stripping/plating potential and steady increase of polarizability with time. This eventual increase in polarizability in the Ca-Sn cell at the later stripping and plating that resembles the Ca/Ca symmetric cells may be related to the instability of the coating at the later cycles, which resulted in the unwanted passivating layer eventually building on the Ca surface as the Ca-Sn breaks and exposes Ca. Rate tests of Ca/Ca symmetric and Ca-Sn/Ca-Sn symmetric cells were

also attempted, as presented in figures 9.3 e and f, which show the large polarizability seen in previous tests for the Ca/Ca cell in the unsuccessful rate testing of the Ca/Ca cell. The Ca-Sn/Ca-Sn cell was successful in being tested at the different rates of 0.1 mAcm⁻², 0.2 mAcm⁻², and 0.5 mAcm⁻², with 0.2 mAcm⁻² operating at the lowest polarizability of the different rates. However, fluctuations of the polarizability during the stripping and plating process may be due to the instability of the electrolyte that was synthesized and utilized for these tests instead of the actual coating's capabilities.



Figure 9.3: a) Comparison of the stripping and plating of Ca/Ca symmetric cell, Ca-Sn/Ca-Sn symmetric cell, and Ca/Ca-Sn asymmetric cells continuously stripped and plated at 0.1 mAcm² for 15 minutes. The isolated data for b) Ca/Ca symmetric cell, c) Ca-Sn/Ca-Sn symmetric cell, and d) Ca/Ca-Sn asymmetric cell are also presented. The rate test of e) Ca/Ca symmetric cell and f) CaSn/Ca-Sn symmetric cell at 0.1 mAcm⁻², 0.2 mAcm⁻², and 0.5 mAcm⁻² rate are also presented.

9.5 Conclusion

In summary, preliminary tests were done to study the effectiveness of Ca-Sn as a protective coating for Ca metal during the re-plating process. These tests suggest the Ca-Sn coating resulted in slightly higher polarizability of the cell due to a new interface between the Ca metal and Ca-Sn coating, but a more even stripping and plating of Ca, as presented through cyclic

voltammetry. Lifetime and rate tests show the ability of Ca-Sn coating to resist the increasing polarizability of the stripping and plating potential over time as shown for Ca symmetric cells. However, due to the electrolyte instability of the self-synthesized electrolyte salt, the preliminary rate conclusions may need further experimentation to be verified. Future work should focus on identifying a stable electrolyte salt to test the effectiveness of the coating before testing in unstable electrolyte systems. The study of the different passivating surfaces on the Ca-Sn coating may also be of interest, as it may help in further optimizing the experimental design of an effective coating. As research progresses and enables successful stripping and plating of Ca at room temperature with a wider range of electrolytes, the focus will shift towards the production of Ca cathodes, which will help complete the vision of the production of full cell rechargeable Ca metal batteries.

9.6 References

1. Staniewicz, R. J., A Study of the Calcium-Thionyl Chloride Electrochemical System. *J. Electrochem. Soc.* **1980**, *127* (4), 782-789.

2. Aurbach, D.; Skaletsky, R.; Gofer, Y., The Electrochemical Behavior of Calcium Electrodes in a Few Organic Electrolytes. *J. Electrochem. Soc.* **1991**, *138* (12), 3536-3545.

3. Ponrouch, A.; Frontera, C.; Bardé, F.; Palacín, M. R., Towards a calcium-based rechargeable battery. *Nature Materials* **2016**, *15* (2), 169-172.

4. Wang, D.; Gao, X.; Chen, Y.; Jin, L.; Kuss, C.; Bruce, P. G., Plating and stripping calcium in an organic electrolyte. *Nature Materials* **2018**, *17*(1), 16-20.

5. Li, Z.; Fuhr, O.; Fichtner, M.; Zhao-Karger, Z., Towards stable and efficient electrolytes for room-temperature rechargeable calcium batteries. *Energy & Environmental Science* **2019**, *12* (12), 3496-3501.

6. Shyamsunder, A.; Blanc, L. E.; Assoud, A.; Nazar, L. F., Reversible Calcium Plating and Stripping at Room Temperature Using a Borate Salt. *ACS Energy Lett* **2019**, *4* (9), 2271-2276.

7. Ding, M. S.; Diemant, T.; Behm, R. J.; Passerini, S.; Giffin, G. A., Dendrite Growth in Mg Metal Cells Containing Mg(TFSI)2/Glyme Electrolytes. *J. Electrochem. Soc.* **2018**, *165* (10), A1983-A1990.

8. Davidson, R.; Verma, A.; Santos, D.; Hao, F.; Fincher, C.; Xiang, S.; Van Buskirk, J.; Xie, K.; Pharr, M.; Mukherjee, P. P.; Banerjee, S., Formation of Magnesium Dendrites during Electrodeposition. *ACS Energy Lett* **2019**, *4* (2), 375-376.

9. Wang, M.; Jiang, C.; Zhang, S.; Song, X.; Tang, Y.; Cheng, H.-M., Reversible calcium alloying enables a practical room-temperature rechargeable calcium-ion battery with a high discharge voltage. *Nature Chemistry* **2018**, *10* (6), 667-672.

10. Liang, X.; Pang, Q.; Kochetkov, I. R.; Sempere, M. S.; Huang, H.; Sun, X.; Nazar, L. F., A facile surface chemistry route to a stabilized lithium metal anode. *Nature Energy* **2017**, *2* (9), 17119.

11. Zheng, X.; Fu, H.; Hu, C.; Xu, H.; Huang, Y.; Wen, J.; Sun, H.; Luo, W.; Huang, Y., Toward a Stable Sodium Metal Anode in Carbonate Electrolyte: A Compact, Inorganic Alloy Interface. *The Journal of Physical Chemistry Letters* **2019**, *10* (4), 707-714.

12. Chen, T.; Kong, W.; Zhao, P.; Lin, H.; Hu, Y.; Chen, R.; Yan, W.; Jin, Z., Dendrite-Free and Stable Lithium Metal Anodes Enabled by an Antimony-Based Lithiophilic Interphase. *Chem. Mater.* **2019**, *31* (18), 7565-7573.

13. Chen, Q.; He, H.; Hou, Z.; Zhuang, W.; Zhang, T.; Sun, Z.; Huang, L., Building an artificial solid electrolyte interphase with high-uniformity and fast ion diffusion for ultralong-life sodium metal anodes. *J. Mater. Chem. A* **2020**, *8* (32), 16232-16237.

14. Forero-Saboya, J.; Davoisne, C.; Dedryvère, R.; Yousef, I.; Canepa, P.; Ponrouch, A., Understanding the nature of the passivation layer enabling reversible calcium plating. *Energy & Environmental Science* **2020**, *13* (10), 3423-3431.

APPENDIX A

SUPPORTING INFORMATION

10.1 CHAPTER 2 – UNDERSTANDING THE ELECTRODEPOSITION OF PURE PHASE CRYSTALLINE SnSb FROM DEEP EUTECTIC ETHALINE SOLUTION AND ITS APPLICATION AS A LITHIUM-ION ANODE



Figure S2.1: Electrodeposition from 50 mM SnCl₂·2H₂O and 50 mM SbCl₃ in ethaline at a) -0.6 V and b) -0.7 V vs Ag/Ag⁺. XRD patterns (left) and SEM images (right) of the surface of the deposition were used study the crystallinity of the film. At -0.6 V, an amorphous material is made and a polycrystalline deposition is seen on the surface through SEM. Crystalline by XRD and by facets seen on the SEM images prove the deposition of crystalline SnSb at -0.7 V.



Figure S2.2: Cyclic voltammetry was performed on 50 mM $SnCl_2 \cdot 2H_2O$ and 50 mM $SbCl_3$ in ethaline after heated at 110° C. The heating at 110° C were done with the container sealed and unsealed to show if heat itself, or the release of water from the solution resulted in changes with the redox peaks related to Sn.



Figure S2.3: Image of crystalline sol gel forming at the bottom of 50 mM SnCl₂·2H₂O and 50 mM SbCl₃ in ethaline solution heated at 110° C for at least 3 days.



Figure S2.4: Electrical conductivity measurements of 50 mM $SnCl_2 \cdot 2H_2O$ and 50 mM $SbCl_3$ in ethaline at different stages of heating. The solutions' conductivity was studied based on a) the time the solution was exposed to room temperature conditions and b) the temperature of the bath.



Figure S3.1: Galvanostatic cycling of electrodeposited SnSb, Sn, and Sb in half cells. Sudden increase in capacity at about cycle 120 of Sb is due to unexpected interruption of the ARBIN battery cycler.



10.2 CHAPTER 3 – ELECTRODEPOSITION OF PURE PHASE SnSb EXHIBITING HIGH STABILITY AS A SODIUM-ION BATTERY ANODE
Figure S3.2: Images of SnSb electrode surface after different electrochemical conditions using the scanning electron microscope. Images were taken at x500, x5k, and x25k magnification.





Figure S3.3: (Top left) Galvanostatic cycling of electrodeposited SnSb and different Sn-SnSb compositions leading to pure Sn. (Top right) Graph extrapolated from galvanostatic cycling showing when the different composition electrodes fall below 80% capacity retention. Electrodepositions of the Sn:SnSb compositions were done using different Sn:Sb concentrations in ethaline and verified using EDS. (Bottom) dQ/dV graph extrapolated from the galvanostatic cycling showing the sodiation and desodiation events present for different Sn:SnSb electrodes. The red box highlights the presence of a new electrochemical activity at this rate that grows proportionally with the increase of Sn content, suggesting this event is unique to non-SnSb tin.



Figure S3.4: *Ex-situ* X-ray diffraction patterns (left) taken pristine SnSb, after sodiation, and after its first desodiation. The SnSb was cycled galvanostatically to 0.01 V vs Na/Na⁺, held potentiostatically for 5 hours or when current reaches nA, and galvanostatically charged to 1.5V vs Na/Na⁺, then held potentiostatically for 5 hours or when current reaches nA. This test was done to verify crystalline SnSb does reform during desodiation after becoming amorphous during sodiation.

10.3 CHAPTER 4 – UNDERSTANDING THE KINETIC LIMITATION DURING INSERTION-





Figure S4.1: dQ/dV of the SnSb vs Na cell at C/10 rate during its initial cycling (red), and after testing at higher current rates (purple). This figure is shown is done to verify the overpotential seen at higher rate testing is not due to SEI formation.



Figure S4.2: Tafel plot of a SnSb vs Na half-cell. Highlighted in red is related to the sodiation/desodiation of Sb at around 0.8 V vs Na/Na⁺, and in blue the sodiation/desodiation of Sn at around 0.45 V vs Na/Na⁺.



Equivalent circuit model for fitting EIS data. R1 is the electrolyte resistance, R8 is the chargetransfer resistance, Yo10 is the double layer capacitance, and W9 is the Warburg element.

Comparing Sn, SnSb, and Sb when discharged (sodiated) to 0.4 V

	R1	R8	W9	Yo10	a11	Goodness	of Fit
	ohm	ohm	S*s^(1/2)	S*s^a		Chi^2	
Sn	3.996	1.06E+03	3.84E-04	6.24E-06	8.75E-01	1.00E-03	
SnSb	5.542	2.70E+03	9.55E-04	6.50E-06	8.87E-01	5.22E-04	
Sb	1.003	3.21E+03	4.54E-04	1.11E-05	7.27E-01	4.67E-03	

SnSb

	R1	R8	W9	Yo10	a11	Goodness of Fit				
	ohm	ohm	S*s^(1/2)	S*s^a		Chi^2	DC Value	DC Units	AC Value	AC Units
OCV	5.279	3.36E+03	6.20E-05	3.91E-06	9.44E-01	4.34E-03	1.00E-08	А	0.00001	A
DIS 0.4V	5.542	2.70E+03	9.55E-04	6.50E-06	8.87E-01	5.22E-04	1.00E-08	А	0.00001	A
DIS 0.01V	4.465	2.47E+03	1.74E-03	6.81E-06	8.80E-01	4.69E-04	1.00E-08	А	0.00001	A
CH 0.4V	5.777	1.34E+03	1.07E-03	6.14E-06	8.91E-01	1.55E-03	1.00E-08	А	0.00001	A
CH 1.5V	3.821	1.58E+03	1.10E-04	4.64E-06	8.94E-01	1.27E-03	1.00E-08	А	0.00001	A

	R1	R8	W9	Yo10	a11	Goodness of Fit				
	ohm	ohm	S*s^(1/2)	S*s^a		Chi^2	DC Value	DC Units	AC Value	AC Units
OCV	7.116	828.1	1.07E-04	5.89E-06	9.00E-01	7.57E-04	1.00E-08	A	0.00001	A
DIS 0.4V	3.996	1.06E+03	3.84E-04	6.24E-06	8.75E-01	1.00E-03	1.00E-08	A	0.00001	A
DIS 0.01V	4.306	1.02E+03	1.72E-03	7.79E-06	8.60E-01	1.21E-03	1.00E-08	A	0.00001	A
CH 0.4V	6.872	862.6	9.38E-04	5.61E-06	8.83E-01	4.45E-03	1.00E-08	A	0.00001	A
CH 1.5V	5.372	1.72E+03	1.96E-04	4.99E-06	8.80E-01	9.89E-04	1.00E-08	А	0.00001	А

Sb

	R1	R8	W9	Yo10	a11	Goodness	of Fit			
	ohm	ohm	S*s^(1/2)	S*s^a		Chi^2	DC Value	DC Units	AC Value	AC Units
OCV	1.346	3.30E+03	8.05E-05	9.79E-06	7.38E-01	1.30E-02	1.00E-08	А	0.00001	А
DIS 0.4V	1.003	3.21E+03	4.54E-04	1.11E-05	7.27E-01	4.67E-03	1.00E-08	A	0.00001	A
DIS 0.01V	7.18E-01	3.12E+03	4.10E-04	1.09E-05	7.26E-01	4.42E-03	1.00E-08	A	0.00001	A
CH 0.4V	6.31E-01	3.07E+03	4.22E-04	1.07E-05	7.27E-01	4.25E-03	1.00E-08	A	0.00001	A
CH 1.5V	13.36	3.85E+03	1.30E-04	2.67E-06	8.52E-01	1.06E-03	1.00E-08	А	0.00001	A



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Figure S4.3: Nyquist plot of the EIS data from SnSb, Sn, and Sb at 0.4 V vs Na/Na⁺, where Na-Sb is predicted to have occurred but Sn has yet to sodiate.



Figure S4.4: Nyquist plot of the EIS data from SnSb, Sn, and Sb at the fully sodiated state (0.01 V vs Na/Na⁺).



Figure S4.5: dQ/dV of the SnSb vs Li cell at C/10 rate during its initial cycling (red), and after testing at higher current rates (purple). This figure is shown is done to verify the overpotential seen at higher rate testing is not due to SEI formation.



Figure S4.6: Tafel plot of a SnSb vs Li half-cell. Highlighted in red is related to the lithiation/delithiation of Sb at around 0.95 V vs Li/Li⁺, and in blue the lithiation/delithiation of Sn at around 0.62 V vs Li/Li⁺.



Equivalent circuit model for fitting EIS data. R1 is the electrolyte resistance, R8 is the chargetransfer resistance, Yo10 is the double layer capacitance, and W9 is the Warburg element.

SnSb

	R1	R8	W9	Yo10	a11	Goodness of Fit				
	ohm	ohm	S*s^(1/2)	S*s^a		Chi^2	DC Value	DC Units	AC Value	AC Units
OCV	50.18	680.5	4.95E-04	8.52E-06	8.98E-01	1.66E-04	1.00E-08	А	0.00001	А
DIS 0.7V	7.075	581.2	2.87E-03	1.13E-05	8.84E-01	8.57E-05	1.00E-08	А	0.00001	А
DIS 0.01V	6.858	329.5	4.94E-03	2.76E-05	8.13E-01	6.81E-03	1.00E-08	A	0.00001	A
CH 0.8V	6.76	263.7	4.01E-03	1.79E-05	8.37E-01	4.89E-03	1.00E-08	A	0.00001	А
CH 1.5V	5.89	354.5	4.93E-04	1.81E-05	8.19E-01	1.93E-03	1.00E-08	А	0.00001	А

Sn

	R1	R8	W9	Yo10	a11	Goodness of Fit				
	ohm	ohm	S*s^(1/2)	S*s^a		Chi^2	DC Value	DC Units	AC Value	AC Units
OCV	9.79	525.7	7.91E-05	1.19E-05	8.65E-01	4.56E-03	1.00E-08	А	0.00001	А
DIS 0.7V	6.378	712.3	3.42E-04	8.65E-06	8.78E-01	3.69E-03	1.00E-08	A	0.00001	A
DIS 0.01V	32.23	516.8	2.20E-03	3.87E-05	7.48E-01	9.74E-04	1.00E-08	A	0.00001	A
CH 0.8V	17.94	202	1.30E-03	9.76E-06	8.69E-01	1.16E-02	1.00E-08	A	0.00001	A
CH 1.5V	11.47	215.7	3.27E-04	7.84E-06	8.78E-01	1.59E-03	1.00E-08	А	0.00001	А

	R1	R8	W9	Yo10	a11	Goodness of Fit				
	ohm	ohm	S*s^(1/2)	S*s^a		Chi^2	DC Value	DC Units	AC Value	AC Units
OCV	19.57	139.5	3.21E-04	5.95E-06	9.26E-01	1.44E-02	1.00E-08	А	0.00001	A
DIS 0.7V	8.741	184.6	1.46E-03	1.06E-05	8.85E-01	2.49E-02	1.00E-08	А	0.00001	А
DIS 0.01V	14.12	193.4	8.31E-04	1.15E-05	8.71E-01	1.40E-02	1.00E-08	А	0.00001	А
CH 0.8V	7.498	193	1.30E-03	1.11E-05	8.78E-01	2.72E-02	1.00E-08	A	0.00001	A
CH 1.5V	7.621	160.5	3.97E-04	7.49E-06	9.04E-01	2.81E-02	1.00E-08	А	0.00001	А



Figure S4.7: Nyquist plot of the EIS data from SnSb, Sn, and Sb at 0.7 V vs Li/Li⁺ during lithiation and 0.8 V vs Li/Li⁺ during delithiation, where Li₃Sb and Sn is present.



Figure S4.8: Nyquist plot of the EIS data from SnSb, Sn, and Sb at the fully lithiated state (0.01 V vs Li/Li⁺).



Figure S4.9: XRD patterns (left) of the in situ cell, in situ cell including cell parts excluding the SnSb electrode, and the full in situ cell at pristine state prior to cycling. The XRD patterns help

verify diffraction peaks related to the in situ electrochemical cell, verifies the peaks related to Cu and Na, and peaks present for SnSb. The (*) are extra peaks that were formed after exposure of Cu/Na/Separator and electrolyte to air while removing SnSb from the cell prior to the XRD run. The in situ cell setup is shown (right) to explain the expected presence of Na and Cu in the XRD pattern.



Figure S4.10: Ex situ XRD patterns of the SnSb electrode prior to cycling and after sodiation and desodiation in the in situ electrochemical cell (setup described in figure S4.9).

10.4 CHAPTER 5 – UNDERSTANDING THE ELECTRODEPOSITION OF Sn-Sb THROUGH AQUEOUS SOLUTION FOR HIGH MASS LOADING LITHIUM-ION ANODES

10.4.1 Initial pulse-rest depositions (based off of pre-pulse rest potential)

Initial depositions through aqueous solutions were performed near pH of 7 due to the preliminary electrodepositions suggesting a decrease in the presence of crystalline Sn in this region. Pulsing sequences were required as shorter pulses allows for better control of nucleation and growth, increasing adion on the surface that results in more nucleation sites rather than continuous growth from limited sites of nucleation seen during constant deposition. Shortening of deposition pulses maximizes concentration of adion on surface, while resting time allows for replenishing of adion used during previous pulse.

Constant current deposition pulses were initially performed, as it allows for control of thickness and mass of the active material if rate of deposition can be obtained. However, constant current depositions did not allow for the deposition to reach great enough negative reducing potential, leading to Sb-rich depositions that fall short of Sn deposition and led to the formation of Cu2Sb. XRD of constant current pulse deposition films resulted in Sb with minor impurities of Cu₂Sb and Sn-Sb.



Chronoamperometric electrodepositions were performed to allow for more consistent codeposition of Sn and Sb, as more negative potentials than seen in chronopotentiometry can be obtained. Initial chronoamperometry pulse-rest sequences allowed for pulses at desired negative potential, and rest based on open circuit potential of the solution prior to deposition sequence (labeled OCV). When using the pulsing sequence of -0.7 V vs Ag wire for 20s, then OCV 30s for 180 times, XRD presented the presence of a Sb-rich film containing crystalline Sb, and some form of Sn-Sb. Altering to a shorter pulse time for each step to a -0.7V vs Ag wire for 10s, then OCV 30s sequence for 180 times resulted in the appearance of crystalline SnSb with Sb. Reverting to higher pulse time, but less times repeating the cycles (-0.7V 20s, CCV 30s for 90 times) resulted in reverting back to a crystalline Sb sample. This set of experiments suggests the longer pulsing sequence leads to deposition beyond the depletion of adions on the surface of the working substrate. As the surface adions is depleted, electrodeposition onto the surface of the working electrode would then be dependent on the rate of the individual ions in the solution and their ability to reach the electrode surface. Due to a hypothesis of the higher rate of Sb diffusion from the bulk of the solution due to XRD results, deposition of Sb-rich products is found. When pulses were shortened to 10s, crystalline SnSb was present in the product due to the pulse being within a rate at which does not fully deplete all adions near the surface of the electrode.



The pulse-OCV sequence was also tested to observe the effect of the resting time on the resulting product of the deposition. Based on three different sequences due to varying amount of time given prior to the next pulse, XRD patterns of the depositions suggests longer rest lead to more even deposition, and less Sb. Longer rest allows for adions near the surface of the electrode to replenish, leading to more even deposition, as verified by the diffraction patterns. Due to less time allowed to replenish Sn and Sb ions present near the surface, sequences with less rest resulted in the reliance on the diffusion of the individual ions from the bulk to the surface of the electrode electrode. Again, this lack of balance between the amount of time for pulse and rest results in uneven deposition of the ions present, resulting in the presence of Sb when sequence allows for less rest.



10.4.2 Why pouch cells were used instead of coin cells?

Initial electrochemical tests were intended to be performed in coin cells. However, initial galvanostatic cycling resulted in cells that quickly failed. The initial cycles saw a continuous dip in capacity with each successive cycle, and cells lose most of its capacity after 3 cycles. The differential capacity plot showed expected electrochemistry, which verified SnSb electrodes undergo the expected Sn and Sb lithiation events. However, once disassembled, the cell was found to have used up all of its electrolye, showing it's the coin cells' limitation to provide sufficient amounts of electrolyte to lithiate/delithiate the high surface area electrodes.





10.4.3 Why choose pH 7.4 vs pH 7.25 with constant stir?

Solution at pH 7.4 as opposed to a slightly lower pH of 7.25 was prepared for the production of SnSb due the resulting product being closest to 1:1 Sn:Sb. The following results describes the products through pulse deposition with constant stir was performed in the different pH Sn-Sb solution. Through utilizing a pH 7.27 solution, the XRD pattern of the electrodeposited product results in crystalline SnSb and Sn. SEM images of the surface of this product observes nodular and less crystalline growth at certain regions of the electrode surface. EDS of this surface results in a 3:2 Sn:Sb ratio, which suggests a more Sn rich environment at this region when compared to the 5:4 Sn:Sb ratio found at pH 7.4.





10.4.4 Effect of reference used on CV and electrodeposition

Experiments were performed to test the effect of the reference used and how it affects the products found on the electrodeposited film. The following depositions were performed using a 50mM SbCl₃, 50mM SnCl₂·2H₂O, 176mM sodium citrate, 400mM citric acid solution tuned to pH 7.4 using KOH. Deposition potential of the products shown was determined based on the highest reductive current peaks present in the CV's prior to the deposition. Depositions were performed a -0.7 V vs reference for 10s, rest for 30s for 200 cycles. Depositions mentioned in this paper were based off of using the Ag wire submerged directly into the solution. What was discovered through these experiments is that the CV reference potential was slightly shifted after depositions when using Ag wire submerged directly into the deposition solution. While the references with the Ag wire placed in a glass cell is very consistent (0.17 vs SCE) with what is shown with SCE, depositions using these reference electrodes were still inconsistent in targeting the 1:1 Sn:Sb. Electrodeposition were performed on and between the reduction peaks present, and still showed less consistent production of the 1:1 Sn:Sb product on foams. Due to the higher likelihood of forming between 5:4 to 1:1 Sn:Sb products, electrodeposition was continued by using the Ag wire submerged directly into the solution. What stayed consistent with all three reference electrode used are the redox events present throughout depositions. After every deposition, the potential of the reduction peaks not only shifted, but the number of reduction peaks differed (where this differing of reduction peaks were consistent with all reference). We hypothesize this change with reduction peaks may be due to drastic changes with the deposition solutions, where the huge change/depletion in ion concentration greatly affects the redox seen.





10.4.5 Thin Film depositions in Sn-Sb aqueous solution

Experiments were performed using a 50mM SbCl₃, 50mM SnCl₂·2H₂O, 176mM sodium citrate, 400mM citric acid solution tuned to pH 7.4 using KOH. These sets of experiment were originally tested to identify the ideal deposition potential for the depositions on Ni foam. Presented below is the CV prior and after deposition from the solution. Unlike CV of the solution during deposition onto Ni foam, the CV obtained from the solution does not change with 300 seconds of constant potential depositions, showing the drastic change in solution with the foam deposition. The CV remains the same when comparing prior to depositions to after 6 depositions. Depositions were performed between the range of -0.95 V vs SCE and -1.3 V vs SCE, to identify the ideal conditions for the thin film depositions around the reduction peaks present. At -0.95 V, a very broad set of peaks were present showing the onset to the formation of SnSb, but minor broad Sb peaks are also present at 40° and 42° 20. From -0.95 V to -1.2 V vs SCE, pure crystalline SnSb was found present. At -1.3 V, Sb, again, is found present in the deposition in concurrent to the

formation of SnSb. Due to these results, the ideal range to for deposition of pure crystalline thin SnSb films is believe to be between -0.95 V and -1.2 V vs SCE, with the most crystalline films at -1.05 V.





10.4.6 CV vs Sn aqueous and Sb aqueous compared to SnSb aqueous

Experiments were performed comparing the CV of the Sn-Sb solution, prior to depositions, to solutions containing only Sn and only Sb in separate solutions. The solutions containing the individual Sn and Sb species contained only one reduction event coupled with an oxidation event. The reduction event presented in the Sn solution occurs at -1.075 V vs SCE, with the oxidation occurring at -0.235 V. For the Sb solution, the reduction event is present at -1.02 V, with matching oxidation peak at -0.23 V. These redox events in the individual solutions do not match perfectly with the reduction peaks presented in the Sn-Sb solution. In the Sn-Sb solution, the CV presented two reduction peaks present at 0.995 V vs SCE and 1.11 V. While the less negative reduction peak in the Sn-Sb solution may match the peak in the individual Sn solution, the more negative reduction peak does not match (-1.11 V vs -1.02 V, respectively) with the individual Sb solution.



10.5 CHAPTER 6 – DEVELOPMENT OF A 3D ARCHITECTURAL DESIGN FOR HIGHER STABILITY ANODE –INVESTIGATION INTO THE ELECTROPOLYMERIZATION OF A POROUS POLYANILINE (PANI) AS A CONDUCTIVE AND MECHANICALLY STABLE BACKBONE

The following are SEM images not presented in the main text that may help reveal the conclusions

we made throughout this article.

Additional samples altering the concentration of H₂SO₄ and aniline in the polymerization solution:



0.05M H₂SO₄, 0.5M aniline 50mA for 1800s on Ni. (1:20 H⁺:Aniline)



0.05M H₂SO₄, 0.5M aniline 50mA for 1800s on SnSb coated Ni foam. (1:20 H⁺:Aniline)



0.05M H₂SO₄, 0.5M aniline 100mA for 3600s then 150mA for 3600s on SnSb coated Ni foam. (1:20 H⁺:Aniline)



0.05M H₂SO₄ 0.2M aniline solution polymerization sequence of 150mA for 5s, then 20 seconds of rest repeated for 1440 cycles on SnSb coated Ni foam. (1:8 H⁺:Aniline)



0.5M H₂SO₄ 0.5M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 120 cycles on SnSb coated Ni foam. (1:2 H⁺:Aniline)



0.5M H₂SO₄ 0.5M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 180 cycles on SnSb coated Ni foam. (1:2 H⁺:Aniline)



Additional experiments performed in varying degree of light

0.2M H₂SO₄ 0.2M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 150 cycles on SnSb coated Ni foam with indirect light. (1:2 H⁺:Aniline)



 $0.2M H_2SO_4 \ 0.2M$ aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 180 cycles on SnSb coated Ni foam with indirect light. (1:2 H⁺:Aniline)



0.2M H₂SO₄ 0.2M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 150 cycles on SnSb coated Ni foam directly in light. (1:2 H⁺:Aniline)



0.2M H₂SO₄ 0.2M aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 100 cycles on SnSb coated Ni foam directly in light. (1:2 H⁺:Aniline)



 $0.2M H_2SO_4 0.2M$ aniline solution polymerization sequence 0.8V for 5 seconds, rest for 15 seconds repeated for 220 cycles on SnSb coated Ni foam directly in light. (1:2 H⁺:Aniline)

10.6 Additional Supporting Experiments



Figure S7.1: Coulombic efficiency versus cycle number of the different composite electrodes that were galvanostatically cycled. This zoomed in version shows the key differences in coulombic efficiency within the 98 to 100% range.