A comparative study of tin anodes in carbonate and glyme electrolytes

Ameya Tushar Khirwadkar

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A COMPARATIVE STUDY OF TIN ANODES IN CARBONATE AND GLYME ELECTROLYTES

Ameya Tushar Khirwadkar

A THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Aerospace Systems Engineering to The Graduate School of The University of Alabama in Huntsville May 2024

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Abstract

A COMPARATIVE STUDY OF TIN ANODES IN CARBONATE AND GLYME ELECTROLYTES

Ameya Tushar Khirwadkar

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Aerospace Systems Engineering

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Sodium-ion batteries (SIBs) are a focus of novel energy research as they present a sustainable alternative to lithium-ion batteries (LIBs) due to the abundance of sodium and anode materials. Tin is a promising option for anodes in SIBs because of its ability to be used independently or with other metal alloys. The advantage of using styrene butadiene rubber in tin anodes is a source of intrigue for potentially improving the shelf life of anodes and reducing the electrical fatigue on the battery. The study of glyme electrolytes compared to widely used carbonate electrolytes can potentially improve cycling life and the overall performance of the battery. Copper current collectors are the default when it comes to battery anodes but with the low reactivity of sodium with aluminum and its thermal stability, the comparison shows the difference in the charging-discharging capacities which potentially reduces cost. The test cells are subjected to ex-situ material characterization (X-Ray Diffractometry) to study the anode material and electrochemical tests (Galvanostatic Cycling for Potential Limitation, Electrochemical Impedance Spectroscopy and Cyclic Voltammetry) to understand internal electrochemical processes.
of the batteries. The specific charging-discharging capacities of the cells showed a benefit to aluminum current collectors over copper. An advantage to glyme electrolytes was observed over the 10-cycle period, with significantly lower cell degradation in long-term cycling tests. Impedance responses for short-term cycling showed cell degradation over stepped potentials and fluctuating responses which are accounted to the formation of SEI layer during the initial cycling phase of SIBs. CV results exhibit the evolution of electrochemical activity which are supported by GCPL results.
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Chapter 1. Introduction

1.1 Operation of a Battery

The basic function of a battery is to convert chemical energy to electrical energy by harnessing electrochemical reactions occurring at two electrodes: a positive and a negative electrode, which are widely referred to as cathodes and anodes respectively. The controlled reduction-oxidation (redox) reactions on the active materials in the battery is what gives rise to an electrochemical potential that is used to power devices. At the end of the electrodes, current collectors act as conductors within the battery that bridge the connection between the electrode materials and the external circuit as well as act as proponents for the electrode materials. The electrolyte serves as an intermediary between the electrodes that facilitates the transfer of charges, essentially converting stored chemical energy into working electrical energy. The electrolyte consists of a solvent and a salt that provides the medium for the flow of ions in the battery. For decades, the go-to base material for rechargeable (secondary) battery production in commercial applications has been lithium ion (Li⁺) as it offers a high energy density and specific energy storage option. However, from research in battery technology over the years, there have been developments in other options for electrochemically active ions such as sodium (Na⁺), potassium (K⁺) and magnesium (Mg²⁺) batteries, which are part of the family of different alkali-ion batteries.
From Figure 1.1 it is observed that an electrode consists of two main parts: the current collector and electrode coating. The current collector is generally battery grade copper or aluminum foil, which, as the name suggests, collects and redistributes the electronic charges during the redox reactions. The electrode coating is fabricated of three constituents: an active material, conductive additives and a binder to hold the active material and conductive additives together. The active material (e.g., graphite, silicon, tin, or a metal oxide) holds the necessary ions while the conductive additive facilitates electron transport through the electrode. The binder is dedicated to hold these components together in a matrix which includes pores of various sizes that distribute electrolyte across the electrode. There are two fundamental directions in which charge travels across a battery. A conventional lithium-ion battery is described in Figure 1.1 to
understand the charging and discharging processes. In a discharged battery, the metal ions are present in the cathode, which makes it the source of the active ions and is necessary for converting electrical energy into chemical energy. When the battery is charged for the first time, metal ions from the cathode, or the positive electrode, migrate to the electrolyte. This results in an oxidation reaction at the cathode and is called delithiation in lithium-ion batteries (LIBs) or desodiation in sodium-ion batteries (SIBs). The electrolyte simultaneously sees an increase in the concentration of metal ions, which then intercalate into the negative electrode, or anode, where a reduction reaction takes place.

During the initial cycles, there are relatively a smaller number of metal ions that are transferred between the electrodes because of the formation of a solid electrolyte interphase (SEI) and cathode layer interphase (CEI) at the cathode and anode respectively. The SEI is a thin layer of precipitate formed due to the reaction between metal ions and the electrolyte, forming an amalgamation of fluorides, oxides or carbonates, which is a few nanometers thick. The composition of the SEI is dependent upon the composition of the electrolyte. Since this phenomenon is inevitable, the battery must be designed taking its formation into consideration, as the loss of ions and electrolyte for the layer eventually leads to a loss in battery capacity. This layer, however, is found to be very useful in alkali-ion batteries as it is responsible in improving the stability, cycle life, and performance of the battery.

1.2 Motivation for Batteries

The recent need for renewable sources of energy has accelerated due to the increasing global demand for energy associated with increasing standards of living and
concerns with climate change associated with the past use of fossil fuels. Contemporary research takes a multifaceted approach to harnessing renewable energy, storing and distributing it effectively for many diverse purposes. Each link of the chain must be safe, economical and viable for future use.

With the ever-growing need for energy consumption, and the simultaneous depletion of fossil fuel sources, the shift to alternative fuels has taken environmental consciousness seriously. Developmental efforts are made to build farms for renewable sources such as wind and solar for which batteries have become a healthy and cleaner option for energy storage. Development of batteries with higher energy densities and shelf lives helps improve the sustainability for energy storage and eventually reducing the dependency on non-renewable energy.

The advancement in personal and commercial transportation has been making a transition to using cleaner fuels to reduce the daily carbon footprint. Electric vehicles (EVs) are an industry making quick strides in developing various models with better operating range, performance and charging times and are made to run on a variety of terrains. This transition helps reduce pollution and reliance on fossil fuels. However, this doesn’t completely make us independent from using fossil fuels as they still make up some percentage of electricity production [1]. Figure 1.2 compares the carbon dioxide emissions between vehicles running on internal combustion engines (ICE) and EVs. It is observed that a hybrid sourcing system consisting of different fuels to obtain electricity would be the smartest way to reduce emission levels.
Figure 1.2 The carbon footprint of vehicles depends on the origin of electricity [1].

The integration of large-scale energy power to sustain larger cities and cater to consumers’ peak demands, their construction should be able to efficiently transmit power which requires its design to be cost effective. With the increasing number of product manufacturers that rely on energy storage systems, many countries are aiming to drastically increase their electricity generation from solar and wind farm in this decade, with simultaneously dropping costs in production [2]. Figure 1.3 describes the history in development costs for renewable energy. With non-renewable fuels becoming more expensive, the production costs of establishing solar and wind farms for clean energy looks to be a more reasonable option.
Economic factors and market demands continue to drive motivation for the battery technology development industry. Demand for certain battery specifications, availability of materials and skilled labor are crucial in expanding this industry. For example, to reduce costs of running energy farms, it has been observed to be highly economical to build hybrid [3] wind and solar farms to reduce loads and costs on battery grids. Innovation in battery technology and rapid growth of the industry presents significant opportunities in employment, big investments and global competitiveness between global governments and private entities. On the other side of the coin, the surge in demand for batteries has had severe impact on the material mining. The mining of cobalt, nickel and lithium, among other materials, take place under poor labor supervision, extensive child labor, and hazardous working conditions [4,5]. The European
Chemical Society in 2021 [6] presented an image of the periodic table that helps visualize the mining issues faced to procure these materials (Figure 1.4) which encouraged the shift to renewable or other sources which are available in abundance. Lithium extraction requires large amounts of groundwater to collect the ores, which reduces the amount of water available to the people in surrounding areas for their agricultural and personal use. These issues raise ethical questions about the moral justification in mining materials and whether the sacrifices made are worth it. Scientists also investigate sustainable alternatives into the chemistries of batteries such as sodium-ion batteries, which may have fewer liabilities in exploiting nature or human lives.

![The 90 natural elements that make up everything](image)

**Figure 1.4** Alternatives to heavily mined elements are available for research [6].

While the motivation for battery development is multifaceted, addressing performance, device portability, environmental and humanitarian concerns is overwhelming. However, with technology improvements and awareness among
consumers becoming apparent, a sustainable trade-off is to be found which will pave the way to a greener future.

1.3 Why Sodium-ion Batteries?

Sodium-ion batteries are standing out as a desirable alternative to lithium-ion batteries mainly due to the significant abundance of their key material, sodium, in the form of soda ash [7]. Figure 1.5 describes the availability of sodium in Earth’s crust and is clear of other options. Since both kinds of batteries run on the same principle, the same manufacturing process can be used for sodium batteries, reducing the manufacturing costs significantly. While lesser than the capabilities of lithium, the volumetric and gravimetric density of sodium makes it an appealing option when used in conjunction with renewable energy sources like wind and solar, and some potential applications in transportation.

Figure 1.5 Availability of elements in the Earth’s crust [8].
The design for sodium-ion batteries is like that of lithium-ion batteries, as both belong to the family of alkali metals. However, the size difference in atomic radius between sodium and lithium does present its own engineering challenges [9] when formulating a favorable combination of electrode materials and electrolyte [10]. Hard carbon anodes have been a popular subject of research for their environmental impact in electrode casting such that manufacturing low-cost options which use Earth abundant materials make them sustainable in the long term. One ingenious study proposes the synthesis of hard carbon by carbonization of fruit shells [11] and calcinating them at high temperatures which resulted in batteries with relatively high specific discharge capacities and coulombic efficiencies, which indicate a potential solution for partially biodegradable batteries in niche applications. Other researched options in transition metal or metal oxide anodes focus on increasing the redox potentials and energy density of sodium-ion batteries [12,13]. To improve the conductivity of the anodes and ensuring a homogenous mixture of components, the use of additives and binders are an important part of research.

Organic binders such as carboxymethyl cellulose is a widely used binder in anode design. Additional binders may also be used to improve the structure of the anode which reduced delamination in storage or during electrochemical testing, increasing the overall life of the test cell. The choice of electrolytes is a critical chemical component to ensure near-ideal performance of sodium-ion batteries. An effective electrolyte facilitates the transport of sodium ions during charging and discharging cycles, improves battery life and determines resultant battery performance, which is influenced by performance parameters such as energy density, cycling life and coulombic efficiency. Different
electrolyte phases like solid, liquid or gel [14] are some options being considered based on the battery application.

A crucial motivation factor for industries to start adopting sodium-ion technology are the cost benefits. Sodium is widely available and can be extracted from abundant sources such as seawater and salt mines. The bulk of lithium raw material, on the other hand, has an uneven global distribution, and the supply chain for Li-ion batteries and lithium refineries for EVs and conventional battery storage methods is similarly imbalanced [15]. The abundance of sodium makes the decision to pursue this route an appealing option, especially to manufacturing sodium batteries in a larger scale. Li et al. conducted a cost analysis study between LIBs (NMC622 cathode and graphite anode) and SIBs (Na\textsubscript{2/3}Fe\textsubscript{1/2}Mn\textsubscript{1/2}O\textsubscript{2} cathode and hard carbon anode) in 2020 for the individual components in batteries; the cost breakdown comparison is described in Figure 1.6. They revealed that in addition to using less expensive materials, increasing the energy density of the active material is crucial to achieving low-cost sodium-ion batteries [9].
1.4 Objectives and Overview

Sodium-ion batteries (SIBs) have emerged as a promising alternative to the conventional lithium-ion battery (LIBs) in energy storage research. With the energy needs of the world increasing every day alongside the unsustainability of non-renewable resources such as fossil fuels, exploring different materials and technologies have become a focus for research groups. Sodium-ion batteries have emerged as a potential contributor to this more sustainable energy mix. The chemistry behind the working of sodium-ion batteries is analogous to that of lithium-ion batteries in that an active material in one
electrode disperses ions transferring through an electrolytic medium. The ions are transferred via ion intercalation into the material of an opposing electrode. The fundamental difference between the two battery chemistries is the different alkali metal ion. However, this also impacts selection of key battery materials. For example, hard carbon is more amenable to sodium storage than graphite. Similarly, tin shows better sodium storage capability than silicon as a high-capacity material. The lack of electrochemical alloying activity between sodium and aluminum means anodic current collectors do not have to be made of copper.

The objective of the thesis is to compare sodium-ion battery performances when introducing variation in multiple components. This comparison is achieved by observing how these variations affect the electrochemical performance and structural and cycling stability of the battery. The observations are obtained from a series of experiments studying the performance of sodium-ion batteries assembled from different combinations of two crucial components, namely the anodic current collector and the electrolyte. With sodium-ion batteries also being compatible and non-reactive with aluminum, the performance potential of using different current collectors is a focus for the study. The use of additives in the binder of the anode is also considered. Ionic transfer in a battery is not possible without an efficient electrolyte. This thesis compares a widely used carbonate solvent with glyme solvents, which have shown less toxicity in their application. Different sodium salts are experimented with electrolyte formulations in this study. While sodium-perchlorate (NaClO₄) salt was widely studied with carbonate-based electrolytes, literature study revealed that using sodium hexafluorophosphate (NaPF₆) in glyme solvents did not result in significant changes compared to the perchlorate salt,
leading to the decision for the latter being the proposed formulation. While using an organic binder in the casting process of the electrode is essential, there is a possible need for an additional component to improve on its shelf life and subsequently a better cycling life of the battery.

The thesis covers the benefits of adopting sodium-ion batteries and their potential applications in different industries and the work being done to improve their performance in Chapter 2. The test matrix for experiments conducted and their respective methodologies are discussed in Chapter 3. Chapter 4 analyzes the results from multiple characterization techniques and Chapter 5 summarizes the results and concludes the thesis.
Chapter 2. Literature Review

2.1 The Sodiation Process

The transfer of ions in active materials of any battery take place by three working principles: insertion or intercalation, conversion and alloying. The different ion transfer principles can be observed from Figure 2.1 in lithium-ion batteries [16]. Any of these principles can be observed in anode reactions while cathodes are usually subjected to intercalation of charges. Intercalation of ions takes place with the guest charges moving between layers of the host material, which makes the process highly reversible because of a relatively uninterrupted path within the structure. However, this reduces the energy density of the battery compared to other transfer principles. In the case of sodium ion batteries, the transfer of ions between the electrodes are classified into two main processes generally referred to as desodiation and sodiation. Sodiation is the insertion of sodium ions into a host or active material, while the extraction of the same from the active material is desodiation.
It was also observed that sodiation and desodiation is highly reversible in sodium ion batteries that used micro-tin for one of its electrodes. This occurs because of the formation of a compact solid electrolyte interphase (SEI) layer which becomes a proponent for better cycling life and cell performance [17]. Qin et al found that glyme electrolyte with dissolved 1M NaPF6 salts produced a stable and conductive SEI layer which prolonged cycling life in sodium-ion batteries, on the contrary to a carbonate-based electrolyte from SEM results. In another case with graphite anodes in sodium ion batteries, transmission electron microscopy was used to understand the change in anode structure during the sodiation-desodiation process with cyclic voltammetry [18]. The

**Figure 2.1** Different mechanisms of charge insertion in host materials [16].
interlaminar distance within the graphite anode increased when the battery was sodiated compared to a pristine sample, which can be inferred from Figure 2.2.

![Sodiation and desodiation of Super P carbon anode](image)

**Figure 2.2** Sodiation and desodiation of Super P carbon anode [18].

Operando X-ray diffraction is an effective method for observing these processes in real time [19]. This test captures the chemical changes taking place between the electrodes when subjected to electrical current during sodiation and desodiation. One of the first operando methods of studying battery electrodes was done by Chianelli *et al.* in 1978 [20], where they “dynamically” studied the Li/TiS$_2$ cathodes by using continuous X-ray diffraction to record the structural changes in the electrode based on the collected electrochemical data. In-situ X-ray diffraction for sodium ion cells has been successful to understand the alloy phase formations between the sodium and metal ions [21]; X-ray nanotomography being a similar technique to study the structure on a more detailed level [22]. These studies can help understand the structure of the binary phases which affect the electrical conductivity and overall performance of the battery.
2.2 Electrode materials, Binders and Additives

The transfer of ions in batteries takes place between two oppositely charged electrodes: cathode and anode. Both electrodes contain active materials that enable ion transfer. To study the difference in performance based on the composition of an electrode, they are manufactured based on three main ingredients to the matrix: active materials, binders, and conductive additives.

There have been multiple studies for different metallic active materials for electrodes [23], of which one favorable option is tin, because of its high electrochemical capacity and efficiency in charge and discharge capabilities [24]. Studies with alternative metals such as antimony have been a subject of comparison with tin in SIBs [25]. While both options exhibit reversible specific capacity in the 500-700 mAh/g, antimony anodes are observed to be more stable in their cycling performance. However, the abundance of tin over antimony and their lower redox potential than their counterparts which exhibits better energy density make it a more favorable option. Extensions to the use of tin to its alloys has also been a subject of study for both sodium and lithium-ion batteries, such as tin-phosphorus alloys and tin oxides [26], which provide better coulombic efficiency when their particle sizes are reduced to the nanoscale. An amorphous red phosphorus-carbon composite in tin anodes have exhibited a high specific capacity of 1890 mAh/g [27]. However, due to the poor conductivity of phosphorus, it must be compensated by a higher percentage with conductive carbon additive, which reduces the gravimetric and volumetric energy densities, which is a crucial factor to maintain successful battery applications. Hard carbon is also a widely applied active material for sodium-ion battery anodes. Its applications are independent and have also been tested in metallic composites,
with tin for example, in both lithium and sodium-ion batteries [28]. However, electrochemical tests showed that while Na₅Sn alloys formed at lower potentials, sodium ion-batteries exhibit lower cycling capacities and high electrical resistance compared to lithium ions, which occurs because of the larger atomic radius of sodium ions.

The addition of binders and additives to the matrix improves the conductivity of the electrode with conductive additives while binders ensure a homogeneous mixture of the components in the anode slurry. Carbon black is a commonly used conductive additive for many battery types because of its excellent electrical conductivity, chemical inertness and wear resistance, to which the battery is subjected to multiple times while being charged and discharged. The function of using binders while casting electrodes is to bind the individual components homogenously [29]. However, over the cycling tests, electrodes will degrade with time and delaminate off the current collector as it is constantly susceptible to electrical fatigue, affecting the overall battery performance. Sodium carboxymethyl cellulose (CMC-Na) is a commonly used binder in electrode casting as it shows relative higher current density in initial cycles and stabilizes over subsequent cycles, exhibiting robust recyclability in the test cell. Other organic binders such as sodium polyacrylate acids (PAA), sodium alginates (ALG), PVDF and PTFE or a combination of two (PAA and CMC) have shown improvements in the cycling stability and cell performance because of their convenient use in aqueous media as presented by Ma et al [30].

However, the agglomeration of tin particles during cycling tests are observed to be detrimental to the capacity retention [31], limiting the sodiation and desodiation processes and accelerating capacity decay. This led to the testing of cells with an
additional organic binder in styrene butadiene rubber (SBR). The combination of sodium carboxymethylcellulose and SBR have been a common application in casting of graphite anodes in lithium-ion batteries [32,33]. Compared to other advanced inorganic binders that may show better performance [34], CMC with SBR is found to be a great alternative based on the trade off in commercial viability. The solubility of styrene butadiene rubber in water [35] is also a positive factor which bodes well for our case in using a water-ethanol mixture as a solvent for the slurry. This combination of additives showed even dispersion or homogeneity of micro-tin in the slurry, improve the long term cyclability of the test cell and reduced erosion or delamination of anodes inside the test cell and in storage.

The variation in the current collector can introduce a potential alternative to using conventional copper. The primary reason for including aluminum as a current collector would be for its lower cost compared to copper. However, the low reactivity of sodium with aluminum [36] at room temperature and potential for long-term cycling with high coulombic efficiency [37] are also important considerations to make a reversible alternative to lithium-ion batteries. Multiple studies have worked with aluminum current collectors [9,31,38] for their light-weight nature and efficient long-term cycling ability that produced a discharge capacity of 500 mAh/g with tin anodes in sodium-ion batteries. Stability of the anode is necessary to achieve long-term cycling results and the use of different sodium salts for anode casting on aluminum foils presented the hexafluorophosphate salt to be least likely to decompose when used with carbonate-based electrolytes [39], along with reasonable thermal stability of the salt, which could retain its mass up to operating temperatures of 300°C.
2.3 Electrolytes

Electrolytes in batteries are an important part for their functioning as they serve as the medium of conducting ion flow between the cathode and anode. An electrolyte consists of two components: a solvent and a compatible salt. The salt dissociates into an active ion (cation) such as Li$^+$ or Na$^+$, the electrochemically active species that transports charges through the medium, and a counter-ion (anion) such as ClO$_4^-$ or PF$_6^-$, that floats in the solvent acting as a contact ion and improving the stability of the battery [40]. The choice of solvent on the other hand depends on the solubility of the salt and determines the ionic conductivity of the electrolyte. The selection of appropriate electrolyte components depends on the active material in the battery, along with its cost and its environmental impact. Performance parameters such as energy density, stability in cycling, electrochemical window, rate of charge and discharge, and operating temperature range are considered as they are influenced by the choice of electrolyte.

There has been extensive research in the field of developing new electrolyte formulations for studying dendrite growths [41], increasing operational voltage range and enabling batteries to perform optimally under various environmental conditions [36,42,43]. As the scope for alternative options to lithium-ion batteries with other metal-ion batteries is more sought after than before, there also have been studies for polymer-based electrolytes for other options such as sodium-ion and magnesium-ion batteries [44]. However, these new options come with their own advantages and disadvantages in terms of their viability, environmental impact and contribution to battery performance. While liquid electrolytes exhibit advantages in better ionic conductivity and wettability over gel
and solid electrolytes, they also present drawbacks with electrochemical instability and containment risks leading to operational safety and disposal issues.

Carbonate based electrolytes have been extensively applied in electrolyte development in typical alkali ion batteries even though they generate unstable SEI layers when used by themselves. These carbonate-based solutions occur in a combination of two types of solvents: cyclic and linear carbonates. In studies with lithium-ion batteries [45], cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC) or fluoroethylene carbonate (FEC) are shown to stabilize cathode surfaces and provide passivation of anode surface (see Figure 2.3); these solutions also enabled lithium salts to be easily soluble. Linear carbonates like dimethyl carbonate and diethyl carbonate, on the other hand, are less viscous and result in more ionically conductive and stable electrolytes when mixed with the cyclic carbonates. In the case of sodium-ion batteries, the decision on which salt is to be used was made to study the difference in performance as investigations found minimal changes in the battery’s limiting capacities between the sodium perchlorate and sodium hexafluorophosphate salts in carbonate and glyme electrolytes [46].
With some of the focus in electrolyte research in polymeric options, organic solvents that are glyme-based have also been a topic for development for some time. Glymes, or glycol diethers, are a group of non-cyclic saturated polyethers that have no additional functional groups [47]. They have a general formula of \( \text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3 \), and the type of glyme depends on the length of the compound chain, ranging from monoglymes to tetraglymes. Compared to other organic solvents, glymes tend to be less volatile and toxic, which makes them an interesting option when their effect on the environment is concerned. However, they are known to potentially induce health and reproductive damages long-term [48]. Glymes exhibit good thermal and chemical stability which makes them a great option for various chemical applications in the laboratory and industry. Studies with glymes of different chain length revealed the amount of ion association when NaPF6 was dissolved in the solvent [49] via nuclear magnetic resonance (NMR) and EIS measurements. On the extremes tested with
monoglymes and tetracycles, monoglymes presented higher ionic association which led to ion agglomeration and eventually poor dissolution in the electrolyte with poor conductivity. Tetracycles however, exhibited high ionic dissociation but with the higher viscosity of the tetracycle resulted in poor ionic conductivity in the battery. Diglymes, partially presented the best of the two options and is the most viable option amongst the other glyme variants for their better conductivity, because of relatively lower ionic association compared to monoglymes, and compatibility with the sodium hexafluorophosphate salt. To complement the advantages exhibited by glyme electrolytes, the use of micro-sized tin in making anodes have been studied for their favorable properties [50]. Tin is found to have high theoretical specific capacities of 847 mAh/g upon formation of Na$_{15}$Sn$_4$ alloys during cycling [21], an abundance in availability and environment friendliness as discussed in Chapter 1.

For the electrolyte to exhibit strong ionic conductivity, different variety of salts can be dissolved to improve its overall performance [51]. When tin anodes are used in sodium-ion batteries, sodium salts paired with different cations can be used. NaClO$_4$, NaPF$_6$, NaBF$_4$, Na$_2$Ti$_3$O$_7$ [12], are some examples of sodium salts used in different research applications. Of all the available and potential choices of sodium salts, NaPF$_6$ and NaClO$_4$ have been the subject of many electrolyte studies. The use of fluoroethylene carbonate (FEC) as a stabilizing additive with tin anodes in SIBs has shown to have good short-term cycling results with both NaPF$_6$ and NaClO$_4$, especially when applying other carbonates as the primary solvent [51]. Performance of NaPF$_6$ in the diglyme solvent was not that different than using NaClO$_4$ as it forms stable electrolytes [52]. Additionally, the use of 1M of NaPF$_6$ in glyme electrolytes yielded over 90% coulombic efficiency for
long-term cycling tests (over 300 cycles) at room temperature, with minimal formation of
dendrites on the sodium counter electrode [37]. This was achieved because of the
homogenous SEI layer formed by sodium oxide (Na₂O) and sodium fluoride (NaF),
which can block the electrolyte and avoid dendrite formations. Sodium perchlorate salts
are widely experimented in SIBs and are also being studied for applications in other
energy storage systems like supercapacitors [53].

2.4 Safety and Viability

As the development efforts towards sodium-ion batteries are being made, the
issue of their safety and viability is an important consideration. Achieving sustainability
and environmental friendliness for battery production are key for the product to thrive in
the industry. The chemistry of sodium-ion batteries is less reactive than lithium-ion
making it a stable and safer option. However, recycling battery materials is an issue that
is being tackled to reduce its carbon footprint. There are recycling methods in place to
extract materials from lithium-ion batteries but processes such as hydrometallurgy which
are observed to increase eco-toxicity [54]. With increased consumption of batteries in
portable electronics, transporting waste materials from disposed electronics also
contribute to increase in greenhouse emissions contributing to global warming [55].
However, some studies have introduced conventional processes, such as sulfation
roasting that could potentially reduce production and disposal waste in the battery
industry[56]. However, with sulfation roasting known to produce large amounts of sulfur
oxides, Lin et al. [56] proposed a technique to add an additional step before battery
disposal to increase the efficiency of sulfur oxide emissions.
The abundance of sodium in the Earth’s crust enables scalability for large-scale energy storage grids as it is the most promising application of sodium-ion batteries. Sodium-ion batteries offer a compelling combination of safety and viability based on nonflammable electrolytes that are thermally and electrochemically stable [57,58]. The abundance and lesser reactivity of sodium promotes safety while the advancements in performance and scalability offers a viable product in the industry, encouraging a sustainable and economically attractive option to lithium-ion batteries.

The viability of sodium-ion batteries depends on the electrochemical performance, cycling performance and scalability. Researchers over the years have worked to improve the energy density, charging-discharging efficiency and overall performance of the battery and eventually closing the performance gap to lithium-ion batteries.

2.5 Summary

Based on the literature in previous research, tin-based anodes in sodium-ion batteries exhibit the formation of sodium-tin alloys in low electrochemical potential window and are shown to present a theoretical specific capacity of 847 mAh/g. Studies using an aluminum current collector has shown a sustained discharge capacity of 500 mAh/g in SIBs using electrolytes based on carbonate solvents. Copper current collectors showed similar performance in the same electrolyte. The glyme electrolyte in SIBs, namely diglyme, has shown the highest capacity and efficiencies among other glyme variants compared to carbonate electrolytes. The addition of styrene butadiene rubber binder in the slurry formulation of the anode is expected to show better specific capacities, especially in the glyme electrolyte, because of the reduced tin agglomeration
in the anode surface, reducing delamination and improving conductivity of ions in the electrodes with high coulombic efficiency in long-term cycling. Based on the previous work in sodium-ion batteries from the literature study, this thesis aims to add insights to the battery performance, exploring the combinations of electrolytes, current collectors and addition of styrene butadiene rubber.
Chapter 3. Methodology

The process followed for testing different chemical combinations of sodium-ion battery test cells is explained in this section. All anodes applied micron-sized tin as the active material for sodium storage. There are three variable parameters considered in the experiments carried out: changes in binder composition, changes in electrolyte formulation and use of different materials in the current collector.

The experiments are initially established by drawing up a test matrix for the electrode and electrolyte combinations. Section 3.1. Section 3.2 cover the steps followed to prepare these battery components. The anodes for the test cells are casted based on previously worked procedures [29]. The electrolyte preparation and test cell assembly using coin cells is explained in the subsequent sections. Electrochemical characterization of the test cells is carried out after the fabrication procedure. These measurements included Galvanostatic Cycling with Potential Limitation (GCPL) followed by Electrochemical Impedance Spectroscopy (EIS) and Cycling Voltammetry (CV). X-Ray Diffraction tests are conducted on the pristine anode samples to verify the retention of tin structure when mixed in a homogenous slurry with additives and binders. Table 3.1 describes the materials used for the experiments.
Table 3.1 Materials list for characterization of tin-based sodium-ion anodes.

<table>
<thead>
<tr>
<th>MATERIALS LIST</th>
<th>Electrode Fabrication</th>
<th>Electrolyte preparation</th>
<th>Cell Assembly</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tin, powder, 10micron, 99%, Sigma-Aldrich</td>
<td>Sodium perchlorate salt (NaClO₄), Sigma-Aldrich</td>
<td>Whatman ® glass microfiber, GF/C separator</td>
</tr>
<tr>
<td></td>
<td>70%</td>
<td>1.0 M</td>
<td>Sodium chunk, Fischer Scientific</td>
</tr>
<tr>
<td></td>
<td>Super C65 Nano Carbon Black additive, MSE</td>
<td>Propylene Carbonate, Sigma-Aldrich</td>
<td>Fabricated anode</td>
</tr>
<tr>
<td></td>
<td>20% (15%)</td>
<td>50%</td>
<td>Prepared electrolyte 200-250μL</td>
</tr>
<tr>
<td></td>
<td>Carboxymethyl Cellulose (CMC) binder, MSE</td>
<td>Fluoroethylene Carbonate, Sigma-Aldrich</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Styrene-Butadiene Rubber (SBR) binder, MSE</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(5%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Deionized water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Battery Grade Copper Foil, MSE</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Battery Grade Aluminum foil, MSE</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.1 Test Matrix

The experiment for this thesis focuses on studying the performance of sodium-ion batteries based on different chemical combinations of the components in test cells. The variables for the series experiments are:

1. Type of current collector foil
2. Addition of styrene butadiene rubber (SBR)
3. Electrolyte

The test matrix followed for the experiments are covered in Table 3.2.

Table 3.2 Test matrix.

<table>
<thead>
<tr>
<th>Electrolyte [Salt (Solvent)]</th>
<th>Current Collector</th>
<th>Addition of SBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO4 (PC:FEC)</td>
<td>Aluminum</td>
<td>Yes</td>
</tr>
<tr>
<td>NaClO4 (PC:FEC)</td>
<td>Aluminum</td>
<td>No</td>
</tr>
<tr>
<td>NaClO4 (PC:FEC)</td>
<td>Copper</td>
<td>Yes</td>
</tr>
<tr>
<td>NaClO4 (PC:FEC)</td>
<td>Copper</td>
<td>No</td>
</tr>
<tr>
<td>NaPF6 (DEGDME)</td>
<td>Aluminum</td>
<td>Yes</td>
</tr>
<tr>
<td>NaPF6 (DEGDME)</td>
<td>Aluminum</td>
<td>No</td>
</tr>
<tr>
<td>NaPF6 (DEGDME)</td>
<td>Copper</td>
<td>Yes</td>
</tr>
<tr>
<td>NaPF6 (DEGDME)</td>
<td>Copper</td>
<td>No</td>
</tr>
</tbody>
</table>

3.2 Test Cell Fabrication

The fabrication of a test cell requires three components: the active material anode, electrolyte and a counter electrode, either sodium metal for a half-cell or an active material cathode for a full-cell. The anode and electrolyte are prepared in the laboratory based on formulations from previous experiments and literature as explained in Chapter 2. The anode casting process is done few days prior to the assembly inside a fume hood to reduce exposure to any harmful gases. The electrolyte and final cell assembly however
are done inside an inert argon environment to limit contact with moisture and other contaminants.

### 3.2.1 Casting of the Anode

The anode for testing cells is manufactured inhouse and this process begins with the preparation of a slurry containing active material of tin. Tin powder with a 10-micron average particle size and 99% purity by Sigma Aldrich is used in this build as the active material, with SUPER C65 Nano Carbon Black powder as a conductive additive and battery grade Carboxymethyl cellulose (CMC) as an electrode binder. Carbon black is chosen as an additive for its high conductive property and sodium carboxymethyl cellulose as the binder whose aqueous solvability contributes to a homogeneous slurry mixture.

A slurry of 3g is prepared in which the active material, additive and binder is mixed in the weight ratio of 70:20:10 [29]. Deionized water was initially used as the solvent for the slurry. The slurry components are run in a vortex mixer (Figure 3.1 (a)) for an hour with eight glass beads to ensure an even mixture. However, cracking of the electrodes was observed in storage over time. The ineffectiveness of using just CMC as a binder is drawn as the conclusion for this defect. It was observed that the CMC took longer than expected to be mixed properly in the slurry. To improve on this drawback, the CMC is dissolved in a mixture of 70% deionized water and 30% ethanol about a week prior to being added to the mixture. A quantity of 13-15mL of pre-mixed CMC is added to the tin-carbon additive mixture to obtain a satisfactory consistency of the slurry.
An additional binder in styrene butadiene (SBR) is studied to analyze the qualitative and quantitative difference it contributes to the cycling performance of the test cells. The SBR made up for 5% of the slurry at the expense of carbon black, which helps improve the structural integrity of the electrode and keeps it intact for longer [31]. The compositions of the electrode materials are recorded in Table 3.3 and Table 3.4. The numbers 6-9 are used as indicators of the sample type for ease of tracking during measurements. The theoretical values shown were the target compositions for the electrode mixtures.

**Table 3.3** Anode casting without SBR additive.

<table>
<thead>
<tr>
<th>Anode Index</th>
<th>Tin (g)</th>
<th>Carbon Black additive (g)</th>
<th>Pre-mixed CMC binder (g)</th>
<th>Solvent (0.7 H2O:0.3 EtOH) (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>2.100</td>
<td>0.600</td>
<td>0.300</td>
<td>-</td>
</tr>
<tr>
<td>6 (Aluminum)</td>
<td>2.140</td>
<td>0.601</td>
<td>0.300</td>
<td>15</td>
</tr>
<tr>
<td>8 (Copper)</td>
<td>2.110</td>
<td>0.602</td>
<td>0.300</td>
<td>15</td>
</tr>
</tbody>
</table>

**Table 3.4** Anode casting with SBR additive.

<table>
<thead>
<tr>
<th>Anode Index</th>
<th>Tin (g)</th>
<th>Carbon Black additive (g)</th>
<th>Pre-mixed CMC binder (g)</th>
<th>SBR additive (g)</th>
<th>Solvent (0.7 H2O:0.3 EtOH) (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>2.100</td>
<td>0.450</td>
<td>0.300</td>
<td>0.150</td>
<td>-</td>
</tr>
<tr>
<td>7 (Aluminum)</td>
<td>2.210</td>
<td>0.452</td>
<td>0.300</td>
<td>0.160</td>
<td>15</td>
</tr>
<tr>
<td>9 (Copper)</td>
<td>2.106</td>
<td>0.455</td>
<td>0.300</td>
<td>0.186</td>
<td>15</td>
</tr>
</tbody>
</table>

Following mixing, the slurry mixture is then casted on an aluminum or copper current collector foil, whose surface is wiped with isopropanol before using a doctor blade set to a wet film thickness of 200 micron (Figure 3.1 (b)). The drying process for the anode started at room temperature for around 12 hours followed by drying in a vacuum oven at 70°C for 16 hours. The dry film thickness of the anodes is measured
using a Mitutoyo Thickness gauge (Figure 3.1 (c)) with the least count of 1 micron. An average thickness of the casted anode across is surface is considered for specific capacity calculation.

![Figure 3.1](a) Mixing slurry using a vortex mixer (b) Casting slurry on copper current collector using a doctor blade (c) Mitutoyo Thickness Gauge.

### 3.2.2 Preparation of Electrolytes

Two different electrolyte types are studied: carbonate and glyme-based electrolytes. Both electrolytes are prepared in-house from as-received salt and solvent materials. The methodology and formulations for the electrolytes are described as follows:

**Carbonate electrolyte**

The sodium perchlorate electrolyte is a commonly used electrolyte in sodium-ion test cells. For the formulation of the electrolyte, 1 M of sodium perchlorate (NaClO4) salt is added to a solvent mixture of 95% polyethylene carbonate (PC) and 5% fluoroethylene carbonate (FEC). This mixture is moderately heated over a heating element until the salt is completely dissolved and left to rest overnight.
Glyme electrolyte

A glyme-based organic electrolyte is tested as an alternative to the carbonate electrolyte as to how it affects the capacity of test cells. Diethylene glycol dimethyl ether (or diglyme) from Sigma Aldrich is used as the base for this electrolyte. By default, the manufacturer maintains fewer than 50 ppm of moisture in the diglyme, however, the dehydration of the solvent is needed to reduce the chance of water reacting with the other components of the battery assembly [59]. According to extensive empirical evidence by organic chemists working with drying their solvents [60], the organic solvent is dehydrated over a prolonged period of exposure to molecular sieves.

Before the solvent could be dehydrated, molecular sieves from Sigma Aldrich, 3 Å pore size and 8-12 mesh, are to be activated. Molecular sieves in 5-10% weight per volume is dried overnight in a vacuum oven at 200°C and are subsequently left to rest for about one hour. In an argon environment, 20 mL of diglyme solvent and molecular sieves are left untouched for 48 hours. After the dehydration process, the solvent is separated from the sieves and one mole of sodium hexafluorophosphate salt is mixed to maintain one molality solution [61]. This mixture is carefully heated over a heating element until the salt is completely dissolved and left to rest overnight for it to become usable for test cells.

3.2.3 Assembly of Test Cells

The test cell can be assembled one of two ways: half-cell or full-cell configuration. A half-cell tests an individual electrode while a full-cell test both the cathode and anode within the same system. Figure 3.2 describes both assembly
configurations. The half-cell configuration consists of the test electrode assembled opposite to an ion source, such as a sodium or lithium foil, as a counter electrode to provide ions for electrochemical reactions and subsequent storage in the working electrode. Since an electrode can be studied independently, the half-cell is often used in laboratories to understand individual redox reactions of one specific working electrode, e.g., a composite anode or cathode containing an active material. Full-cells, on the other hand, provide a complete electrochemical cell that consists of a casted cathode instead of a sodium disc, where one half undergoes oxidation and the other half reduction. Full-cells are generally the blueprint for practical batteries used for commercial applications, as the replicate a full operational battery. The cells assembled for this thesis used the half-cell configuration with coin cells and ECC-STD EL-Cell test cells. The tin electrode is the cathode of the half-cell while the sodium foil is the anode. However, the tin electrode is referred to as the anode in this thesis because of its practical application in a full-cell battery.

![Diagram of Full-cell and Half-cell configurations](image)

**Figure 3.2** Full-cell and half-cell configurations.
The test cells for GCPL tests are assembled in an argon environment (i.e., a glovebox with H$_2$O and O$_2$ content < 0.1 ppm) using a 304SS stainless steel CR2032 stainless steel coin cell from MSE Supplies. Each test cell uses a stainless-steel spacer and conical spring to restrict internal movement. The process starts with cutting a thin quadrilateral slice of sodium which is flattened to a desirable thickness of approximately two stacked spacers. The sodium is flattened between two polymer blocks and applying pressure using a C-clamp vise 1/2” electrode is punched from the slice inside the argon environment (Figure 3.4 (c)). The cell is then assembled according to the build direction described in Figure 3.3 and sealed on an Electric Coin Cell Crimping machine (ECCCMM-160E) by MicroNano Tools at a crimping pressure force of 1.30 Torr (Figure 3.4 (a)).

Figure 3.3 (L) CR2032 coin test cell build (R) Assembled Coin cell.
For the EIS and CV tests, EL-Cells (Figure 3.4 (b)) and CR2032 coin cells are assembled for better access to post processing and obtaining concurrent datasets. The EL-cells are also assembled with a half-cell configuration like that of the CR2032 coin cells. However, to make the most of these larger test cells, the amount of electrolyte used increased to $250\mu$L [29].

During the assembly process, some precautions were taken to ensure a consistent test cell build. It was important to keep the punched anodes from curling in vacuum, which occurred most likely due to the contraction from dissolved organic binder. This is achieved by moving the anodes between two plastic trays and assembling each coin cell separately, in case multiple cells are being assembled.

### 3.3 Electrochemical Testing and Characterization

The assembled cells are subjected to electrochemical tests to study internal reactions, chemical performance and cycling life of the battery. These tests help study the sodiation and desodiation processes that take place inside the battery during cycling. The
tests are run within electrochemical boundaries which confine the battery behavior. The data from these tests are analyzed on MATLAB, which plots electrochemical parameters which help visualize the results.

Electrochemical testing of the coin cells consisted of three tests: Galvanostatic Cycling with Potential Limitation (GCPL), Electrochemical Impedance Spectroscopy (EIS), and Cyclic Voltammetry (CV). Only the GCPL tests were run on the Neware CT-4008T 5V10mA Battery Testing System while GCPL, EIS and CV tests are run on the EC Lab software by BioLogic Science Instruments VSP Multichannel potentiostat/galvanostat (see Figure 3.5). The settings for each test are described in the following sections.

**Figure 3.5** Battery Cycling Setup (L) Neware CT-4008T Battery Testing System (R) BioLogic Science Instruments VSP Multichannel potentiostat/galvanostat.
3.3.1 Galvanostatic Cycling with Potential Limitation (GCPL)

Galvanostatic cycling with Potential Limitation is an electrochemical study to understand the cycling behavior of batteries. The study uses an input of charge/discharge rate on the battery and the voltage range in which the battery operates. From these inputs, the battery’s performance is determined as a function of the charging or discharging status. Two systems are used to run the GCPL tests, a Neware CT-4008T Battery Tester and a Bio-Logic VSP multichannel potentiostat/galvanostat. Figure 3.6 describes a sample GCPL plot.

![Figure 3.6 Sample image of GCPL results](image)

The galvanostatic rate is the parameter evaluated to understand the reduction-oxidation reactions occurring at both ends of the battery. This parameter is described as C/h, where ‘C’ is the charge intercalated on either terminal of the battery based on the redox reaction, and ‘h’ determined the time in hours for each step of the process. The specific capacity (mA-h/g) data of the battery from the test are plotted against the
corresponding voltage during the cycling period. However, due to the variation in
electrode composition, individual specific capacities are calculated for corresponding
generated plots. The calculations take the size and material of the casted electrode, and
slurry composition into consideration to determine the amount of stored material
(sodium) in each test cell.

Each test was run for 10 cycles and is subjected to a constant direct current input.
A direct current of ±100 μA is applied to the battery during the charging/discharging
cycle. It is specified on the software to cycle the test cell within the range of 0.01V –
0.8V to display optimal results. Data were recorded every 30 seconds by the cycling
software and exported to a delimited text file.

**Generating plots for GCPL results with a MATLAB Code**

The test cell data for GCPL tests accumulated around 50,000 data points on
average due to long testing times for multiple cycles. To automate the process for
generating plots, a MATLAB code is written which required the input of a delimited text
file with the necessary variables; the variables of cycle number, capacity, voltage and
control current are imported into independent vectors. The current collector thicknesses
are determined theoretically from the product specification sheet while the dry film
thicknesses input measured using the Mitutoyo Thickness gauge is the user input needed
for specific capacity calculations. The MATLAB code for plotting the GCPL results is
presented in the Appendix (A.11).
3.3.2 Electrochemical Impedance Spectroscopy (EIS)

The Electrochemical Impedance Spectroscopy characterization method is used to study the reactions and processes taking place on the electrode interface [62]. Based on the input current, the EIS processes can be broadly classified into two types: AC type for an alternating input and measurements as a function on frequency, and DC type where the response is measured as a function of time. The alternating input is preferred over a direct current because any diffusion due to concentration gradient is negligible and linear input current would create a linear response in impedance hence simplify the testing process [63]. However, working in the time domain can also be done with other electrochemical characterization techniques, like cyclic voltammetry, but analyzing the specimen could prove to be a strenuous task. The main advantage of EIS is to perform quick characterization of the specimen, which is possible because of the wide range of frequencies it offers to adjust the scan rate as required and deconvoluting the spectra based on time constants, simplifying data to be more linear and stable for analysis [64]. In general, the frequency at which the scan is conducted is inversely proportional to the time taken to obtain a single measurement. Most equipment that has EIS measurement capabilities can work within frequencies ranging from 10 μHz to 1 MHz [65] however some exceptions are made depending on the battery to be tested. The EIS measurements for the experiments conducted for this experiment are on a relatively lower range, from 1Hz to 1 kHz, to run a fast scan of the test cells.

The representation of EIS data for AC type is conventionally on a logarithmic scale, where the frequency ratio is measured in units of decades. Nyquist graphs, represented in Figure 3.7, are generated that plot -Im (Z) vs Re (Z), which are the
imaginary and real components of impedance (Z) respectively [65], and a common way of representing EIS results. The imaginary axis of impedance represents the reactive part of impedance which is determined by the capacitance of the circuit while the real axis of impedance presents the resistance of the circuit. Based on the frequency range, it enables the study of mass and charge transfer at the electrodes at different resolutions. While the application of EIS in battery research is extensive, it also has multiple applications to study material corrosion, photovoltaics and organic matter in biology.

For the EIS tests run for this experiment, the frequency range of the test is set between 1 Hz on the lower end up to 100 kHz on the opposite end with 10 points of impedance response being measured per decade for the resultant Nyquist plot, with the sinus amplitude set to 10mV.

![EIS Nyquist plot: (Anode 8 (Copper) in glyme electrolyte)](image)

**Figure 3.7** EIS Nyquist plot: (Anode 8 (Copper) in glyme electrolyte).
3.3.3 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is an electrochemical technique for studying redox reactions. It is an important test in electrochemistry as it allows the study reduction-oxidation reactions, electrochemical behavior, and electrode kinetics at the molecular level [66]. Figure 3.8 depicts a sample CV plot for a SIB using glyme electrolyte [17]. To understand voltammograms, parallels can be drawn from the GCPL plots where the desodiation and sodiation processes can be identified and compared to the corresponding resultant peaks for oxidation and reduction regions.

The x-axis of a CV plot represents the input variable for the system while the y-axis represents the response to the input argument, where the input parameter is applied potential (E in Volts) and current (I in Amperes) is the response measured. The applied potential is swept from a lower voltage limit to an upper voltage limit, referred to as the vertex potentials. These potentials are set to a range that will capture the electrochemical activity of the cell. A scan rate is set to define the how quickly steps of voltage are taken. Peaks in the current output will be observed at relevant potential values for both oxidation and reduction processes. In the present work the test cells were scanned between 0.01 V and 1.5 V vs. Na/Na⁺ at a scan rate of 0.1 mV/s.

The general shape of a CV plot is unique and is characteristic of the relationships between the electrochemical potentials of the cell components and the redox processes occurring between the analytes within the cell. This relationship is mathematically described by the Nernst equation, shown in Equation 3.1 [66].

\[
E = E^0 + \frac{RT}{nF} \ln \frac{Oxidized \ species}{Reduced \ species} \tag{3.1}
\]
Where $E$ is the potential of the cell, $E^0$ is the standard potential, $R$ is the universal gas constant, $T$ is the temperature and $F$ is Faraday’s constant.

![Sample CV plot](image)

**Figure 3.8** Sample CV plot [17].

### 3.4 *Ex-Situ* Material Characterization: X-Ray Diffractometry

X-Ray diffraction is an optical material characterization technique that uses X-ray emissions to study the crystalline structure of a sample. The principle of XRD apparatus is based on the diffraction of emitted X-rays that interfere with one another as they pass through the lattice structure of a sample. This diffraction of X-rays is based on Bragg’s Law, given by Equation 3.2 [67], as proposed by physicists William and Henry Bragg in 1913. This equation explains the correlation between the incident angles ($\theta$) and wavelength ($\lambda$) of the X-rays, with the interatomic distance between the planes of a lattice ($d$):

$$n\lambda = 2d \sin \theta.$$  \hspace{1cm} (3.2)
Figure 3.9 depicts how Bragg’s Law explains the reflection of incident waves on a crystal lattice. The incident waves hit the lattice planes at an angle $\theta$, also called the Bragg’s angle and is reflected off at the same inclination away from the crystal. As previously stated, “d” represents the distance between the interatomic planes of a sample. Since the crystal can contain voids in its structure, the unreflected waves from the surface behave similarly on subsequent planes.

The apparatus used for observing the necessary powders is a Rigaku Miniflex600 diffractometer (see Figure 3.10) and PDXL software to analyze its composition. The samples are tested in a zero-diffraction holder with a 0.2mm deep well. The samples are prepared in the open lab atmosphere as there was minimal risk in exposing non-reactive materials to environmental conditions. A Cu-K$\alpha$ radiation source is used to obtain diffraction patterns with the diffractometer which was expelled at a voltage of 40kV and a current of 15mA. The diffraction pattern for all samples is scanned within the 2$\theta$ range of 10°-100° and recorded data at a rate of 0.01° per second.

![Figure 3.9 Operation of X-Rays following Bragg’s Diffraction Law](image)

**Figure 3.9** Operation of X-Rays following Bragg’s Diffraction Law [67].
Figure 3.10 Rigaku Miniflex600 diffractometer.

An *ex-situ* XRD analysis of the pristine samples are tested to ensure the consistency in structure to that of micro-sized tin manufactured by Sigma Aldrich. The morphology of the micro-sized tin powder is nearly spherical [68] and the results from the XRD tests are discussed further in Chapter 4. The samples are prepared by grinding dried electrodes on a mortar and pestle until a fine micron-sized powder is achieved (see Figure 3.11 (a)). This process was performed under the fume hood to avoid any contaminants from the environment. The powder is transferred into the sample holder such that the well is filled to the brim. The holders are placed inside the X-Ray diffractometer and are held down magnetically (see Figure 3.11 (b)).
Figure 3.11 (a) Sample preparation for XRD (b) Samples set up for X-Ray Diffraction experiment.
Chapter 4. Data and Analysis

4.1 Anode Casting and Electrolyte preparation

Since multiple different combinations of electrode compositions are studied, four electrodes are casted for the test cells, two electrodes each based on the type of current collector and the conditional addition of styrene butadiene rubber additive in each pair of electrodes. Table 4.1 summarizes the composition ratios and physical characterization of every electrode casted for the experiment.

Table 4.1 Summary of electrode material composition and characteristics.

<table>
<thead>
<tr>
<th>Anode Number</th>
<th>Tin (g)</th>
<th>CB (g)</th>
<th>SBR (g)</th>
<th>Solvent (mL)</th>
<th>Current Collector</th>
<th>Dry film thickness (micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.14</td>
<td>0.601</td>
<td>0</td>
<td>15</td>
<td>Aluminum</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>2.21</td>
<td>0.452</td>
<td>0.16</td>
<td>15</td>
<td>Aluminum</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>2.11</td>
<td>0.6092</td>
<td>0</td>
<td>15</td>
<td>Copper</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>2.106</td>
<td>0.455</td>
<td>0.186</td>
<td>15</td>
<td>Copper</td>
<td>50</td>
</tr>
</tbody>
</table>

The solvent is a 70:30 volume to volume ratio of deionized water and ethanol which was premixed with a carboxymethyl cellulose binder to achieve a homogeneous mixture. The wet film thickness on every electrode was set to 200 microns on the doctor blade. However, all anodes were reduced to ~50 micron thickness after drying, regardless of the addition of an extra binder in SBR. All anodes were left to initially dry inside a fume hood for 16 hours at room temperature and subsequently dried in a vacuum oven at 70°C for 12 hours. The dry film thickness was measured after this drying process using the Mitutoyo thickness gauge. An average of the dry film thickness around the usable region of the casting is considered as the input for the MATLAB code to generate plots.
In some previous cases where the slurry lacked solvent or an SBR additive, some cracking and delamination of the surface of the casting is observed which led to following the described process to ensure a good quality of casting. The quality in the four casted electrode sheets is summarized in Table 4.2.

**Table 4.2** Representation of Casted anodes.

<table>
<thead>
<tr>
<th>Anode 6</th>
<th>Anode 7</th>
<th>Anode 8</th>
<th>Anode 9</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="Anode6.png" alt="Image" /></td>
<td><img src="Anode7.png" alt="Image" /></td>
<td><img src="Anode8.png" alt="Image" /></td>
<td><img src="Anode9.png" alt="Image" /></td>
</tr>
<tr>
<td>Aluminum Current Collector</td>
<td>Aluminum Current Collector</td>
<td>Copper Current Collector</td>
<td>Copper Current Collector</td>
</tr>
<tr>
<td>No SBR additive</td>
<td>With SBR additive</td>
<td>No SBR additive</td>
<td>With SBR additive</td>
</tr>
</tbody>
</table>

The preparation procedure for the glyme electrolyte needed a small batch of 20mL solvent mixed with sodium hexafluorophosphate salt to obtain a 1 molality solution. The glyme solvent used was the diethylene glycol dimethyl ether (DEGDME), anhydrous 99.5% diglyme variant from Sigma Aldrich. The default moisture content in this solvent is <50ppm. To start with a solvent with moisture content fewer than 10ppm, it was dehydrated using 3Å pore size molecular sieves for 48 hours [60]. After the addition of NaPF6 salt, a heating element was needed to accelerate the dissolving process.
to achieve maximum homogeneity in the electrolyte. The mixture is stirred constantly at 50°C for 30 minutes and left overnight on the heating element at 30°C.

During the cell assembly procedure, it was observed while adding the electrolyte, using a micropipette tip with a capacity of 200μL, that the glyme electrolyte was less dense than the perchlorate salt electrolyte. This can be confirmed from their safety data sheets, where the 1:1 mixture of PC and FEC is 1.345g/cc, while the density of the diglyme solvent by itself is 0.939g/cc at a room temperature of 25°C. Comparing the diglyme electrolyte to the perchlorate salt electrolyte visually, the glyme electrolyte is observed to be mildly murky with a yellow tint even after the mixing over a long period of time. Additionally, because of the use of molecular sieve pellets for the dehydration process, some residue left by the molecular sieve pellets during the drying process needs to be extracted from the electrolyte to avoid getting the particles in the test cells. This is achieved by carefully decanting the electrolyte into another storage bottle. Figure 4.1 describes the prepared carbonate and glyme electrolytes.

Figure 4.1 Electrolytes (L) NaClO₄ in PC:FEC and (R) NaPF₆ in DEGDME.
4.2 Material Characterization: X-Ray Diffraction

This characterization technique calls to initially establish a datum for the electrode samples based on the structure of tin. The pristine electrodes are tested using an X-Ray diffractometer against pure micron-sized tin powder. The reference peaks of micro-tin and the electrode samples are described in Figure 4.2. The samples were tested simultaneously within the same 2θ range from 10° to 100° with a scan rate of 0.01°/second. Consistent collection of major diffraction peaks at 30-32°, 44-47° and 63-65° confirm the retention of tin even with the addition of other binders and additives. Further qualitative analysis of the samples confirmed a tetragonal structure of tin based on the lattice parameters with a variation of less than 1% in three-dimensional space.

![Figure 4.2 Intensity peaks of Micro-tin and electrode samples.](image)
The intensity peaks of the XRD test for the pristine samples coincide with that of a Tin (CSD data_9008570) reference from the Crystallography Open Database (COD), whose peaks and corresponding Miller indices are shown in Figure 4.3. The red arrowheads mark the major diffraction peaks as analyzed from the PDXL software used in conjunction with the X-Ray Diffractometer. All anode samples show low change in chemistry and structure after casting compared to the active tin material. However, a drop in almost half the intensity is observed for some diffraction peaks of the casted samples. This occurs likely due to the addition of carbon black additive and other organic binders like CMC and SBR, as well as residual particles of copper or aluminum foil while crushing the dried slurry during the sample preparation process.

![Figure 4.3 Tin (CSD data_9008570) peak data.](image)

**Figure 4.3** Tin (CSD data_9008570) peak data.
4.3 Cycling Life

All samples were cycled at a constant current of 100μA between the voltage range of 0.01V-0.8V for 10 cycles, which had an initial C-rate of about C/7. However, five cells from carbonate and glyme electrolytes are subjected to long-term cycling. The cycling behavior of a test cell assembled using the electrode Anode 9 (Copper_SBR) with the carbonate-based electrolyte is described in Figure 4.4. The general behavior of sodiation and desodiation is observed consistently from the figure throughout the cycling process. The effect of cell degradation can be observed from Figure A.1 and A.2 (see Appendix), where the charging and discharging capacities start fading with each subsequent cycle, particularly after ~600 hours using carbonate electrolytes, which is between the 35th - 45th cycle on average. The glyme-based samples however, cycled for longer and completed 50 cycles with minimal capacity loss unlike their electrolyte counterparts, which started showing degradation ~40 cycles earlier.
Figure 4.4 Representative of longer-term cycling data for a tin-based sodium-ion half cell (Anode 9 (Copper_SBR)) in carbonate-based electrolyte.

The fading of specific capacities and capacity retention of the long-term tests are compared to understand its effect on other electrochemical characterizations. Five cells were run long-term (for 100 cycles) of which two, Anode 7 (Aluminum_SBR) and Anode 8 (Copper) in glyme were run for 50 cycles. The first 50 cycles are analyzed in Figure 4.5. Anode 7 (Aluminum_SBR) and 8 (Copper) in glyme show an increase in capacity after the fifth cycle, peaking near the 30th cycle and gradual degradation until the 50th cycle, with a capacity retention of 58.8% and 57.3% respectively. The results from the carbonate electrolytes on the other hand retain a capacity of 35.3% in Anode 6 (Aluminum), 23.4% in Anode 8 (Copper) and 25.3% in Anode 9 (Copper_SBR). A drop in specific capacity during discharge is observed in carbonate electrolyte of below 233.3 mAh/g compared to 699.69 mAh/g and 532.56 mAh/g in Anode 7 (Aluminum_SBR) and
Anode 8 (Copper) in the glyme electrolyte, which is in the expected in range of 500-700 mAh/g. Anode 7 (Aluminum_SBR) in the carbonate-based electrolyte however showed poor capacity retention and irregular behavior until the end of its life. The result of this behavior can be observed in Figure A.4 in the Appendix. The full long-term cycling plots for the samples are shown in the Appendix from Figure A.3 through Figure A.8.

**Figure 4.5** (a) Capacity retention and (b) discharging capacity fade in long-term cycling (50 cycles).

### 4.4 Electrochemical Characterization

#### Galvanostatic Cycling Potential Limitation

The GCPL tests are conducted on the Neware CT-4008T battery cycling system using on CR2032 coin cells based on the assembling procedure described in Section 3.2.3. Multiple batches of cells are prepared for each anode to obtain concurrent data which eventually amounted to sixty coin cells in total. Every coin cell is cycled 10 times within the potential boundaries of 0.01V and 0.8V by applying a constant current of 100μA, which corresponds to an average initial C-rate of C/10. The data post-cycling is
exported and plotted using the MATLAB code described in Section 3.3.1. The specific capacities, calculated based on the dry film thickness and current collector material, are plotted against voltage for the entire duration of the cycling process. The difference in the data is characterized based on the effect between the current collector material, electrolyte and addition of styrene butadiene rubber (SBR). The charging and discharging capacities of coin cells for each sample is shown in Figure 4.6 and Figure 4.7.

![Graphs showing specific capacity plots for different anodes with and without SBR addition.](image)

**Figure 4.6** GCPL specific capacity plots using carbonate electrolyte.
The specific capacities for every sample are compared for both charging and discharging cycles based on the variables presented in Chapter 3. This describes the charge or discharge capacity of the coin cell per gram of active material in each individual cell. The degradation in cell chemistry is observed with the decreasing charging and discharging capacities every subsequent cycle. An average of three replicate coin cells is considered and compared to understand the charging and discharging capacities for all test configurations.

Figure 4.6 compares the maximum charging capacities of the four different anode formulations using carbonate-based electrolyte and with those assembled with glyme electrolyte in Figure 4.7. The latter 60% of cycles are considered for all average specific capacities to fairly account for cell degradation after the first four cycles. The difference

Figure 4.7 GCPL specific capacity plots using glyme electrolyte.
in average charging capacity of coin cells across its cycling time based on the electrolyte is in favor of the glyme electrolyte with 593.78 mAh/g compared to 383.07 mAh/g with the carbonate-based electrolyte. However, some variations in performance based on the current collectors are observed. Cells tested using anodes casted on aluminum current collectors and using carbonate-based electrolyte exhibited better charging capacities, performing 35.49% better than anodes cased on copper foils. The addition of styrene-butadiene rubber to the slurry formulation made a difference to this configuration in exhibiting consistent charging capacities throughout the cycling life of 10 cycles, maintaining at least 600mAh/g.

The charging capacities for glyme electrolyte however describe cell degradation in the first few cycles until SEI formation to then stabilize at the end of the test gradually in Figure 4.8 (b). The Anodes 6 and 9 performed better than Anodes 7 and 8, which are rather consistent in building their specific capacities. The difference between using aluminum and copper current collectors, however, is not far off, with only a difference of 4.46% between them.

While using different current collectors with glyme electrolyte did not show much improvement, the selection when using carbonate-based electrolyte is observed to be quite significant from Figure 4.8 (a). Considering the wide use of these solvents in SIB research, the use of aluminum foil could be a motivating factor for improving battery performance and reducing manufacturing costs [9].
Figure 4.8 Comparison of charging capacities using (a) sodium perchlorate salt in carbonate electrolyte (b) sodium hexafluorophosphate salt in glyme electrolyte.

Considering the discharging behavior in the same coin cells (Figure 4.9), the anodes casted on aluminum current collectors had higher average discharge specific
capacities 569.82 mAh/g compared to the copper anodes 375.47 mAh/g with carbonate-based electrolyte. On the other hand, the coin cells using glyme electrolyte showed only a 3.31% difference in discharging capacity for the respective current collectors (685.73 mAh/g with aluminum and 662.98 mAh/g). The high reversible specific capacities over the theoretical limit of 847 mAh/g in the glyme electrolyte from the initial cycles are observed when using micro-sized tin [17]. These elevated capacities are associated with the SEI layer formation in the initial cycling of the tin-based sodium-ion batteries in glyme electrolytes.

The coulombic efficiency of any battery is described as the efficiency of transferring charge across an electrochemical system [69]. Mathematically, it is represented as the ratio of discharging and charging capacity. The efficiency in the first cycle of the coin cells ranged from 68.67% to 88.86%, with anode Anode 8 (Copper) being least efficient combination with the carbonate-based electrolyte and Anode 7 (Aluminum_SBR) being the most efficient using the same electrolyte. However, Anode 7 (Aluminum_SBR) didn’t sustain the efficiency from its first cycle through the cycling period of 10 cycles and dropped drastically relative to the other samples to 87.56% by the end. The retention of capacity however continued an increasing trend resulting with an average of 94.78% with carbonate-based electrolyte and 93.51% with glyme electrolyte by the end of the 10th cycle. It is interesting to note that the average efficiency for the coin cells was 96.8% regardless of the electrolyte halfway through the GCPL test at five cycles. This indicates an increase in capacity retention after SEI formation in the electrolyte and mild cell degradation eventually reducing to the lower 90s by the end of their cycling life. Anode 7 (Aluminum_SBR) in the glyme electrolyte however tends to
keep up with the efficiencies with its carbonate-based electrolyte counterpart. Tables 4.4 and 4.5 summarize the data from Figures 4.8 and 4.9.

**Figure 4.9** Comparison of discharging capacities using (a) sodium perchlorate salt in carbonate electrolyte (b) sodium hexafluorophosphate salt in glyme electrolyte.
Figure 4.10 Evolution of coulombic efficiency of coin cells with (a) NaClO4 in PC:FEC and (b) NaPF6 in DEGDME.
### Table 4.3 Summary of Charging Specific Capacities.

<table>
<thead>
<tr>
<th>Charging Data</th>
<th>NaClO4 salt in PC:FEC</th>
<th>NaPF6 salt in DEGDME</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td><strong>Average of Cycles 6-10 (mAh/g)</strong></td>
<td><strong>Average of Cycles 6-10 (mAh/g)</strong></td>
</tr>
<tr>
<td>Aluminum (6)</td>
<td>575.777</td>
<td>819.222</td>
</tr>
<tr>
<td>Aluminum with SBR (7)</td>
<td>611.797</td>
<td>601.343</td>
</tr>
<tr>
<td>Copper (8)</td>
<td>382.755</td>
<td>613.454</td>
</tr>
<tr>
<td>Copper with SBR (9)</td>
<td>383.309</td>
<td>743.641</td>
</tr>
</tbody>
</table>

### Table 4.4 Summary of Discharging Specific Capacities.

<table>
<thead>
<tr>
<th>Discharging Data</th>
<th>NaClO4 salt in PC:FEC</th>
<th>NaPF6 salt in DEGDME</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td><strong>Average of Cycles 6-10 (mAh/g)</strong></td>
<td><strong>Average of Cycles 6-10 (mAh/g)</strong></td>
</tr>
<tr>
<td>Aluminum (6)</td>
<td>562.720</td>
<td>791.374</td>
</tr>
<tr>
<td>Aluminum with SBR (7)</td>
<td>576.923</td>
<td>580.092</td>
</tr>
<tr>
<td>Copper (8)</td>
<td>374.938</td>
<td>600.071</td>
</tr>
<tr>
<td>Copper with SBR (9)</td>
<td>376.009</td>
<td>725.902</td>
</tr>
</tbody>
</table>

**Electrochemical Impedance Spectroscopy (EIS)**

The Electrochemical Impedance Spectroscopy tests are carried out on the EC Lab software on the BioLogic VSP Multichannel potentiostat/galvanostat. The cells are assembled in half-cell configurations, like that of the GCPL tests as described in the previous section. All cells are run 5 times to study the impedance response of all test variants. The cells are subjected to current at stepped potentials ranging from 0.01V-1.5V
so that the behavior at increasing voltages could be observed. As discussed in Chapter 3, the frequency range of the test is set between 1 Hz and 100kHz, and the sinus amplitude set to 10mV recording the impedance response 10 times every decade for the Nyquist plot. The resultant plots from the tests are described in Figures 4.12 and Figure 4.13 based on the electrolytes used while assembling the cell.

All cases were set up in a single circuit with stepped potentials within the 0-1.5V window. There are three characteristic zones on an EIS plot to understand the electrochemical processes inside of the battery as shown in Figure 4.11 for the first EIS measurement taken at 0.3 V vs. Na/Na⁺. The initial region of an EIS plot represents the high frequencies of the electrochemical processes. The following semicircular region constitutes of the intermediate frequencies. The region before the semicircle on the plot determines the ohmic resistance of the battery [63]. The last region of the EIS curve is the diffusion tail which describes the lower frequencies.

![Figure 4.11 EIS plot of Anode 6 (Aluminum).](image-url)
The results for the anodes assembled in carbonate-based electrolyte are presented in Figure 4.12. Since the tests cells are scanned between 0.01V and 1.5V, the EIS measurements are coincident with voltage values in increments of 0.3V. Anode 6 (Aluminum) exhibits a fluctuating impedance response, which presents the best capacitance and the inherent flow of ions through the battery in its last potential step, which is favorable for a battery which allows free flow of ions and reduces resistance and heat generation within the system. Anode 8 (Copper) and Anode 9 (Copper_SBR) perform very similar to each other, showing a consistent charge transfer resistance of 270 ohms through the EIS test. Potential step 5 in both tests, however, show a drop in charge transfer resistance in the 180-220 ohm range, and show and increased resistance in the fourth series at 1.2V to 270 ohms. Anode 7 (Aluminum_SBR) is an outlier within the set of results for the carbonate-based electrolyte. Potential step 2 exhibits a high resistance compared to the other samples at 260 ohms, with the subsequent steps dropping the impedance behavior significantly. The early degradation of the test cell is evident from the behavior from the third step onwards because of the lower charge resistance and longer diffusion tail. This results from this test matches the coulombic efficiency results obtained from GCPL tests in Anode 7 (Aluminum_SBR) maintaining a lower efficiency throughout its cycling life compared to the other three samples, which exhibited consistent efficiencies over 90% after the SEI formation from the initial cycles.
Figure 4.12 EIS plots for NaClO4 in PC:FEC.

Figure 4.13 presents the EIS plots for samples using the glyme electrolyte. The results with this configuration exhibits large charge transfer resistances compared to the carbonate-based electrolyte. This was observed in tests with complex higher order glymes, like pentaglymes, symmetric sodium-ion batteries [70]. Anode 6 (Aluminum) shows a charge transfer resistance of 590 ohms in the initial step with degradation following soon after. The charge resistance in Anode 9 (Copper_SBR) increases between the first two potential steps from 600 ohms to 1400 ohms. This sudden jump is an indication of the formation of initial SEI layer which is observed from the GCPL analysis for the glyme electrolyte batteries (Figure 4.8 (b) and Figure 4.9 (b)), where a high
irreversible capacity is observed in the initial cycles and stabilizes in the latter 60% of the cycles of the tests. Anode 8 (Copper) behaves like its counterpart with carbonate-based electrolyte where the transfer resistance gradually increases from 4500 ohms to 9000 ohms, with little observed degradation in the battery as the SEI layer is still being formed in the electrolyte. A long-term EIS test would possibly describe the cell behavior after the SEI is formed.

**Figure 4.13** EIS plots for NaPF$_6$ in DEGDME.
Cyclic Voltammetry (CV)

The cells are tested for their electrochemical behavior using cyclic voltammetry to observe voltages for key reduction and oxidation processes in the sodium-ion battery. The anodes are tested to ensure the desodiation and sodiation processes followed suit with that observed with the GCPL tests. All CV tests were run on BioLogic’s Science Instruments VSP Multichannel potentiostat/galvanostat for 5 cycles. The cells are cycled within an electrochemical potential window of 0.1V and 1.5V, with each subsequent cycle having its data being recorded from a 0V reference.

Figure 4.14 shows the CV response for the first cycle for cells assembled with the carbonate-based electrolyte. The constant current curve in the center of the graph at 0.75V occurs because these CV tests are conducted straight after the EIS measurements and need time to start measuring CV data from the specified reference. The formation of oxidation peaks in the 0.5-0.6V range draws some parallels from Figure 4.6 which describes the desodiation steps in the tin electrode during the charging cycle, where the concentration of sodium-ions (Na+) increases with electron ejection. Anodes 8 and 9 using the copper current collector exhibit prominent oxidation and reduction regions compared to the Anodes 6 and 7, which use the aluminum current collector. Looking back at the charging and discharging capacity fade of Anode 7 from Figure 4.5 with long-term cycling, the combination of aluminum current collector and SBR assembled with carbonate-based electrolyte shows a slow start to building capacity in the battery, which explains the unformed oxidation peaks in the CV test in conjunction with the lower coulombic efficiency observed for the same variant in Figure 4.10 (a). Other factors that result in these initial cycles could be the type of test cell used, ECC-STD EL-Cell or
CR2032 Coin Cells, and the difference in C-rate at which the test cells are run. With the C-rate being faster at 0.1 mV/s compared to the GCPL tests, maintaining the same rate can reveal more consistent characteristics between both tests. The evolution of the CV plots for the anodes in carbonate-based electrolytes are shown in Figure A.9 in the Appendix, where the oxidation regions become more pronounced.

![CV plots](image)

**Figure 4.14** CV plot of Cycle 1 for carbonate electrolyte.

From the CV results on the glyme electrolyte, the final cycles of the four anodes are described in Figure 4.15. The electrochemical behavior of Anodes 7 (Aluminum_SBR) and 8 (Copper) are similar, the third desodiation peak during charging
between 0.1-0.2V being minimal, which explains the drop in specific capacities in Figures 4.8 (b) and Figure 4.9 (b). From the GCPL analysis in Figure 4.7 (c) and Figure 4.7 (d), the desodiation peaks become steep, increasing the charge rate, which also indicates the third oxidation peak being underdeveloped in the CV results. From Anodes 6 (Aluminum) and 9 (Copper_SBR), the coincident oxidation peaks also follow the same behavior from the GCPL analysis. The complete CV plots of anodes with the glyme electrolyte are shown in Figure A.10 in the Appendix.

![CV plots](image-url)

**Figure 4.15** CV plot for Cycle 5 in glyme electrolyte.
Comparing the evolution of CV behavior between carbonate and glyme electrolytes across the five-cycle test, Figure 4.16 represents the same for Anode 9 (Copper_SBR). The initialization of the oxidation region in both electrolytes takes place at similar potentials with the glyme electrolyte charging quicker because of its higher specific capacity in the first cycle. As a result, the diffusion of sodium ion (Na+) concentration during desodiation is greater in glyme than the carbonate electrolyte. About halfway through the test at Cycle 3, the desodiation regions start to exhibit more flow of current through the batteries.

**Figure 4.16** Evolution of CV response for Anode 9 (Copper_SBR) in carbonate and glyme electrolyte.
Chapter 5. Conclusion

The objective of this research was to explore different anodic formulations, current collector materials and the potential improvements in performance when using glyme-based electrolytes in tin-based sodium-ion battery anodes. Electrochemical characterization tests of GCPL, EIS and CV were conducted to study the capacity retention, and evolution of the sodiation and desodiation behaviors. Structural characterization of *ex-situ* X-ray diffraction was run on pristine anodes to ensure that the slurry maintained the baseline of micro-sized tin even after using an additional binder to improve the stability of cell performance.

Four anode samples were casted based on anode slurry composition which included an additional organic binder of styrene butadiene rubber (SBR) on two different current collector materials of battery grade copper and aluminum using an active material of 10 micron-sized tin powder. The electrolytes used for this research were a carbonate-based electrolyte which involved sodium perchlorate (NaClO₄) salt dissolved in 95% propylene carbonate and 5% fluoroethylene carbonate solvents, and sodium hexafluorophosphate salt (NaPF₆) in a diglyme solvent of diethyl glycol dimethyl ether (DEGDME).

The *ex-situ* material characterization using X-Ray Diffraction confirmed the retention of tin even with a drop in peak intensity with the results, with coinciding diffraction peaks and corresponding Miller indices for micro-sized tin in the casted anode for sodium-ion batteries.
The cycling tests (GCPL) were successfully run and revealed an advantage to the aluminum current collector, which presented with better specific capacities compared to copper. It was more prevalent when using sodium perchlorate salt in PC:FEC with the specific capacities being 34.10% higher in aluminum for discharging and 35.49% for charging, while using glyme yielded an advantage to aluminum of 4.46% for discharging and 3.31% for charging. The specific capacities based on the glyme based electrolyte however, presented a 29% advantage over the carbonate-based electrolyte. The analysis of coulombic efficiencies for short-term cycling showed capacity retention at the end of 10 cycles to be at least 90% for all tested cases. This trend was replicated in long-term cycling results, which retained similar efficiencies with reduced capacities from the ~40th cycle with carbonate electrolytes. Capacity retention from glyme electrolyte variants enables the long-term (100 cycle) study which could potentially show comparatively lower cell degradation. The evolution of cell stability, reversibility and long-term cyclability opens multiple research opportunities to improve the battery capacity for long-term applications. EIS and CV presented results on the evolution of battery charge transfer resistances and redox reactions which were parallel to the results obtained from GCPL tests. These tests helped verify the electrochemical behavior of the anode and electrolyte combinations from the test matrix, which exhibit specific capacities in the range of 500-700 mAh/g and high coulombic efficiencies after short-term and long-term cycling. The use of styrene butadiene rubber in the anode slurry formulation showed consistency in long term testing with glyme electrolyte for 50 cycles, retaining 57.5% of its capacity and ~90% coulombic efficiency.
The studies above provide an initial comparison of electrolyte formulations and electrode characteristics for tin anodes in SIBs. Several future work opportunities could expand on this comparison. Expansion of the test matrix to explore the remaining combinations of the two sodium salts and electrolyte solvents could be addressed in future studies, as it was observed that these salts and solvents were compatible when used interchangeably [51,52]. Based on the observed consistency in the performance when including styrene butadiene rubber in the anode, longer term cycling tests that span 100-300 cycles could be pursued to understand the cycling behavior and capacity retention better. Optical imaging techniques can provide a qualitative observation and support to the addition of SBR for long-term tests. Optical microscopy and scanning electron microscopy can help observe changes in active material and the delamination of anodes post-cycling. Additionally, a C-rate capability study for future work would produce a more complete understanding of electrochemical behavior in sodium-ion batteries and the effect of electrolyte properties on rate capabilities.
References


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[56] Lin, J., Liu, C., Cao, H., Chen, R., Yang, Y., Li, L., and Sun, Z., “Environmentally Benign Process for Selective Recovery of Valuable...


Figure A.1 Representative of longer-term cycling data for an Sn-based sodium-ion battery anode for the first 400 hours of cycling.

Figure A.2 Representative of longer-term cycling data for an Sn-based sodium-ion battery anode for 400-800 hours of cycling.
Figure A.3 Representative of longer-term cycling data and capacity retention for Anode 6 (Aluminum) in carbonate based electrolyte.

Figure A.4 Representative of longer-term cycling data and capacity retention for Anode 7 (Aluminum_SBR) in carbonate based electrolyte.

Figure A.5 Representative of longer-term cycling data and capacity retention for Anode 7 (Aluminum_SBR) in glyme based electrolyte.
**Figure A.6** Representative of longer-term cycling data and capacity retention for Anode 8 (Copper) in carbonate based electrolyte.

**Figure A.7** Representative of longer-term cycling data and capacity retention for Anode 8 (Copper) in glyme based electrolyte.

**Figure A.8** Representative of longer-term cycling data and capacity retention for Anode 9 (Copper_SBR) in carbonate based electrolyte.
Figure A.9 Cyclic Voltammetry plots with NaClO$_4$ in PC:FEC.

Figure A.10 Cyclic Voltammetry plots with NaPF$_6$ in DEGDME.
A.11 MATLAB Code for GCPL results.

```matlab
% Create a Status counter vector in Excel file before importing the data into
% MATLAB (eg. for this case, Rest=0, CC DChg = 1, CC Chg = 2)

% Use Excel code for status column:
% = IF(B2="Rest",0,IF(B2="CC DChg",1,IF(B2="CC Chg",2)))

clear

% Text file for battery data
BatteryResultsNW =
readmatrix('01232024_SnCBCMC_6_Z2.txt','Delimiter','

% Specify filename here to appear on graph
filename = ('TESTNAME');

% Specify the path to save your results in:
fname = ('FILEPATH');

% Calculation for specific capacity

% Specify the path to save your results in:
t = input("Dry film thickness [including current collector] in micron: ");

% Specify the path to save your results in:
t = t * 0.00001;

% Specify the path to save your results in:
f = input("Current collector material? (C [copper] or A [aluminum])? ",',s');

% Specify the path to save your results in:
if f == "A" % Aluminum current collector
    cct = 12 * 0.00001; % Theoretical current collector thickness in cm
elseif f == "C" % Copper current collector
    cct = 9 * 0.00001;
end

% Specify the path to save your results in:
Vf = 3.14 * (1.27*.5)^2 * (t-cct); % For ½” anode in cc

% Specify the path to save your results in:
rho_mix = 5.429889; % Calculated for 70:20:10 sample in cc

% Specify the path to save your results in:
M = rho_mix * 0.7 * Vf; % in grams
```
%Change column numbers to match variables

cycleNumber = BatteryResultsNW(:,4);
Voltage = BatteryResultsNW(:,7);
CapacitymAh = BatteryResultsNW(:,8);
status = BatteryResultsNW(:,12);

Time = zeros(size(status));
IDX = BatteryResultsNW(:,1);
cycleLabel = "Cycle ";

for I = 1:size(Time)
    Time(I) = 10/3600 * IDX(I);
end

cycleCapacity = cell(4,max(cycleNumber));
cycleVoltage = cell(5,max(cycleNumber));

% Sort Data by cycle number

for i = 1:size(BatteryResultsNW,1)
    for j = 1:max(cycleNumber)
        if cycleNumber(i) == j
            cycleVoltage{4,j} = string(j);
            cycleVoltage{4,j} = strcat(cycleLabel,cycleVoltage{4,j});
            cycleCapacity{1,j}(i) = CapacitymAh(i)/M;
            cycleVoltage{1,j}(i) = Voltage(i);
        end
    end
end

% Charging and discharging Data

for j = 1:max(cycleNumber)
    for k = 1:length(cycleVoltage{1,j})
        if status(k) == 2
            cycleVoltage{2,j}(k) = cycleVoltage{1,j}(k); %Charging data
            cycleCapacity{2,j}(k) = cycleCapacity{1,j}(k);
        elseif status(k) == 1
            cycleVoltage{3,j}(k) = cycleVoltage{1,j}(k); %Discharging data
            cycleCapacity{3,j}(k) = cycleCapacity{1,j}(k);
        end
    end
end
end

cycleVoltage{5,j} = horzcat(cycleVoltage{3,j}, cycleVoltage{2,j});
cycleCapacity{5,j} = horzcat(cycleCapacity{3,j}, cycleCapacity{2,j});
end
end

%Plot data

C = {'k','b','r','g','m',[.5 .6 .7],[.8 .2 .6],[.6 .4 .8] [.3 .7 .9] [.1 .6 .2] [.8 .4 .5]};

for j = 1:max(cycleNumber)

    figure(1)
    hold on
    plot(cycleCapacity{2,j}, cycleVoltage{2,j},'color',C{j},
    DisplayName=cycleVoltage{4,j})
    ylim([0.01 1.2]);
    hold off
    title("Voltage vs Specific Capacity (Charging Data)");xlabel("Specific Capacity(mAh/g)");ylabel("Voltage(V)");
    legend

    figure(2)
    hold on
    plot(cycleCapacity{3,j}, cycleVoltage{3,j},'color',C{j},
    DisplayName=cycleVoltage{4,j})
    ylim([0.01 1.2]);
    title("Voltage vs Specific Capacity (Discharging Data)");xlabel("Specific Capacity(mAh/g)");ylabel("Voltage(V)");
    legend

    figure(3)
    hold on
    plot(cycleCapacity{5,j}, cycleVoltage{5,j},'LineWidth',2.5,'color',C{j},
    DisplayName=cycleVoltage{4,j});
    fontsize(20,"points");
    ylim([0.01 1.2]); xlim([0 800])
    hold off
    title(filename);
    xlabel("Specific Capacity(mAh/g)");ylabel("Voltage(V)");
    legend

    figure(4)
    plot(Time, Voltage)
    ylim([0.01 1.2]);
    title("Cycling Life");xlabel("Time(Hours)");ylabel("Voltage(V)");
Data Analysis:

Specific Capacity

```matlab
SpCap = cell(2,max(cycleNumber));
for j = 1: max(cycleNumber)
    SpCap{1,j} = max(cycleCapacity{1,j});
    SpCap{2,j} = max(cycleCapacity{2,j});
end
SpCap
```

Coulombic efficiency

```matlab
CE = cell(1,max(cycleNumber));
for j = 1: max(cycleNumber)
    CE{1,j} = (SpCap{2,j}/SpCap{1,j}) * 100;
end
CE
```