DISSERTATION

USING X-RAY PHOTOELECTRON SPECTROSCOPY TO UNDERSTAND THE SOLID ELECTROLYTE INTERPHASE FORMATION IN SODIUM ION BATTERIES

Submitted by

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Summer 2022

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ABSTRACT

USING X-RAY PHOTOELECTRON SPECTROSCOPY TO UNDERSTAND THE SOLID ELECTROLYTE INTERPHASE FORMATION IN SODIUM ION BATTERIES

Sodium-ion batteries offer a more sustainable energy storage alternative to lithium while maintaining many of lithium's important characteristics. The solid electrolyte interphase (SEI) forms on the surface of the anode in both sodium and lithium-ion batteries. The SEI effects battery performance, particularly in sodium batteries, and understanding how it forms is critical for developing sodium ion batteries. Chapter I of this dissertation motivates sodium ion batteries, outlines the important differences between sodium and lithium, introduces the SEI, and establishes how the SEI is studied, ultimately placing this work in context with the field. As the SEI is derived from the electrolyte and is affected by electrolyte additives, the small molecule electrolyte additive fluoroethylene carbonate (FEC) is introduced as it is investigated throughout the dissertation. Chapter II explains how X-ray photoelectron spectroscopy can be used to study the SEI, providing examples of important protocols and pitfalls. Chapter III examines SEI formation by correlating electrochemistry from differential capacity with X-ray photoelectron spectroscopy (XPS). It is revealed that SEI species appear as a result of applied chemistry when the small molecule additive FEC is present. Without FEC, the SEI is present without significant electrochemistry in the differential capacity. Chapter IV builds off the results in Chapter III, identifying the conditions of spontaneous SEI formation due to sodium metal reactivity with the electrolyte. The spontaneous formation of the SEI is mitigated by FEC, the role of which is understood to be pre-passivation of sodium metal to prevent further electrolyte decomposition. Chapter V summarizes the work in this dissertation and outlines different directions the work can take moving forward.

ACKNOWLEDGEMENTS

Finishing graduate school has only been possible due to the help from all of my mentors, friends, and family. Foremost I would like to thank Amy Prieto for being my advisor during this process. She has shown me patience and insight for both growing as a scientist as well as a person. All of my friends and the Prieto group old and new have been invaluable in helping me balance work and not-work, thank you all. My Dad, who has been with me every step of the way supporting me to realize my childhood dreams to help save the world (every only-child's dream). To my mom, I know she would be proud of what I have accomplished. A special thanks to Carly Jewell for being downright brilliant and always knowing what experiment I need to do next as well as always pushing me to improve myself. Of course, Oli, for being universally happy and sharing her joy with everyone she meets.

TABLE OF CONTENTS

ABSTRACTii
ACKNOWLEDGEMENTSiv
LIST OF FIGURESvii
I. MOTIVATING SODIUM ION BATTERIES FOR LARGE SCALE ENERGY STORAGE AND THE IMPORTANCE OF STUDYING THE SOLID ELECTROLYTE INTERPHASE1 1.1 Energy Storage Motivation
II. USING X-RAY PHOTOELECTRON SPECTROSCOPY TO STUDY THE SOLID ELECTROLYTE INTERPHASE: CONSIDERING IMPORTANT VARIABLES AND HETEROGENEITY IN SODIUM ION BATTERY SAMPLES. 22 2.1. Introduction. 22 2.2. Fitting SEI XPS Data 26 2.3. Accurate Reporting of Reproducibility 31 2.4. Conclusions. 33 CHAPTER II REFERENCES. 35
III. X-RAY PHOTOELECTRON SPECTROSCOPY AS A PROBE FOR UNDERSTANDING THE POTENTIAL-DEPENDENT IMPACT OF FLUOROETHYLENE CARBONATE IMPACT OF FLUOROETHYLENE CARBONATE ON THE SOLID ELECTROLYTE INTERFACE FORMATION IN Na/Cu ₂ Sb BATTERIES
3.2. Introduction. 38 3.3. Experimental. 43 3.3.1. Electrodeposition of the Cu ₂ Sb Electrode. 43 3.3.2. Battery Assembly and Cycling. 44 3.3.3. X-ray Photoelectron Spectroscopy. 44 3.3.4. Data Analysis. 46
3.4. Results and Discussion
IV. SPONTANEOUS SOLID ELECTROLYTE INTERPHASE FORMATION IN UNCYCLED SODIUM HALF-CELL: USING X-RAY PHOTOELECTRON SPECTROSCOPY TO EXPLORE THE PRE-PASSIVATE OF SODIUM METAL BY FLUOROETHYLENE

.70
.70
.72
.79
.81
.85
.92
.94
11

LIST OF FIGURES

1.1 Li and Na price and global distribution	2
1.2 Diagram of a lithium-ion battery	3
1.3 Li and Na electrode materials plotting their capacity against their voltage	5
1.4 SEM of a nanowire electrodes and lifetime plot with electrolyte additives	9
1.5 Images of sodium soaked in different electrolytes	.10
2.1 XPS spectra of O and Sb	27
2.2 XPS C spectra of slurry electrode, individual components, and cycled battery	.30
2.3 XPS spectra of various C spectra to illustrate heterogeneity	.31
2.4 XPS C spectra used to illustrate statistical analysis	.32
3.1 Differential capacity plots showing how the three potential regions were chosen	47
3.2 Differential capacity plots of the three potential regions	.48
3.3 XPS C spectra of potential region batteries	.50
3.4 Quantification of C XPS data from potential region batteries	.51
3.5 XPS O spectra of potential region batteries	.55
3.6 Quantification of O XPS data from potential region batteries	.56
3.7 XPS Na spectra of potential region batteries	.58
3.8 Quantification of Na XPS data form potential region batteries	.59
4.1 Diagrams of the different uncycled battery experiments and respective images	73
4.2 XPS spectra of uncycled battery experiments	.75
4.3 EIS spectra of uncycled battery experiments	.78
4.4 Lifetime data of batteries from the different electrolyte conditions	.79
S3.1 Image of electrodeposition cell	.94
S3.2 Diagram of Swagelok battery assembly	.95
S3.3 Capacity vs. cycle number plots of different potential region batteries	.96
S3.4 Python code for plotting XPS figures	.97
S3.5 XPS F spectra of potential region batteries1	00
S3.6 XPS Cl spectra of potential region batteries	102
S3.7 XPS Na spectra of pristine sodium metal	103
S3.8 Large window XPS spectra of Na plasmon event in an LPR sample	104
S3.9 XPS spectra for all elements from Sb substrate potential region experiments	106
S3.10 XPS spectra for all elements from Cu substrate potential region experiments1	07
S3.11 XPS spectra for all elements from Cu substrate fully cycled with FEC	108
S3.12 XPS spectra for all elements from Cu substrate fully cycled without FEC	109
S4.1 Before image of Na soaked in electrolyte conditions1	112
S4.2 Images of Teflon array used to study many Na soaked in electrolyte conditions1	113
S4.3 NMR spectra of blackened Na-soaked electrolyte, image included	114
S4.4 XPS C spectra of Na soaked in electrolyte components and sample image	115
S4.5 XPS Cl, F, and Cu spectra of uncycled batteries in different conditions1	22
S4.6 XPS C, O, and Na spectra of Na counter from uncycled battery experiments	123
S4.7 XPS Cl and F spectra from uncycled battery experiments1	125

I: MOTIVATING SODIUM ION BATTERIES FOR LARGE SCALE ENERGY STORAGE AND THE IMPORTANCE OF STUDYING THE SOLID ELECTROLYTE INTERPHASE¹

1.1. Energy Storage Motivation

Generating energy without producing greenhouse gases is a clear step required for combating the ongoing climate crisis.¹ Renewable energy sources such as wind and solar are intermittent, meaning a robust energy storage system and a more electrified society will be require for success.^{2–5} Currently the transportation sector is electrifying, particularly personal vehicles, capitalizing on the emergence of lithium-ion battery (LIB) technology.⁶⁻⁹ In order to assist with intermittent renewable energy, rechargeable, or secondary batteries, will need to fill an expanded niche, beyond transportation, and serve as a large-scale energy storage system. However, the relative abundance of lithium in the earth's crust and its geographical distribution limits its larger scale applications.¹⁰ The majority of lithium needed for lithium ion batteries begins as lithium carbonate, before being used to make various lithium cathode materials.¹¹ Lithium is currently gathered from lakes in Chile, Argentina, and Bolivia as lithium chloride and, secondarily, is mined in Australia as the mineral spodumene before conversion to lithium carbonate.¹¹ Exploitation of South American countries for their natural resources is not a suitable course of action a lesson repeated across history. An alternative source for lithium is seawater, but a low concentration of 0.2 ppm and the excess concentration of sodium makes for a difficult separation challenge and is

¹ This chapter is intended to motivate the work in this dissertation. The chapter references a variety of review articles to give literature perspective and identify where additional research and understanding is required. Portions of this chapter are from published manuscript in *Electrochemical Society: Interface* with Nathan J. Gimble, Kelly Nieto, and Amy Prieto. Nathan J. Gimble and Kelly Nieto equally wrote and edited the manuscript with supervision and additional help from Amy L. Prieto.

the focus of ongoing research.^{12,13} Lithium carbonate price and distribution over the last 20 years is depicted in Figure 1.1 A and B, respectively. Lithium carbonate prices are growing significantly limiting accessibility of battery technology. Ultimately a different, more sustainable battery system will be needed for the scale at which renewable energy will be stored to power a world run without fossil fuels.



Figure 1.1. A) Price of lithium and sodium carbonate from 2005 to 2019, inset: price percent change. B) Distribution and amount of lithium and sodium around the world. Graphics from Hirsh et. al. 2020.¹⁴

There are many different beyond lithium battery technologies.¹⁵ From a sustainability point of view, sodium is the clear choice for an alternative to lithium. Sodium is the 6th most abundant element in the earth's crust and can also be used to make batteries using the same electrochemical principles as lithium.^{10,16} A comparison between lithium and sodium carbonate abundance and price is shown in Figure 1.1. Sourcing sodium for battery applications will likely be through sodium carbonate or soda ash as a starting material for sodium cathodes. Gathering sodium carbonate is much more sustainable than its lithium counterpart as it has greater geographic distribution. Sodium chloride is found abundantly in nature, with sodium making up 3.5% of seawater and is widely mass produced via evaporation, then there are multiple industrial scale chemical reactions available to convert it to sodium carbonate.^{17,18} This is to illustrate that sodium

ion batteries are a clear sustainable choice for an electrochemical energy storage system at a scale that can be coupled with green renewable energy production.

1.2. Sodium and Lithium-ion Battery Function

Lithium and sodium-ion batteries work analogously to one another and, like other electrochemical cells, have three parts: the anode, the cathode, and the electrolyte.^{19,20} Lithium and sodium-ion batteries are rechargeable with reversible electrochemical redox reaction that occur at each electrode. During discharge, electrons flow from the anode to the cathode and can do work as this is a spontaneous process. Lithium or sodium ions flow through the electrolyte to charge balance the two redox reactions occurring at the two electrodes. An applied voltage can drive the reverse redox reactions flowing electrons from the cathode to the anode along with the subsequent lithium charge balancing. This process is depicted in Figure 1.2.



Cathode Electrolyte and Separator Anode

Figure 1.2. Graphic of a lithium-ion battery at an intermediate state of charge adapted from the US department of energy.¹⁹ The cathode is on the left in green, electrolyte is the blue background, separator is the black line in the middle, and the anode is on the right. Lithium ions are labelled, and electrons are yellow balls. The state of charge is shown in the meter on the far left.

Lithium has been developed as a battery because it is very attractive as an electrochemical storage device due to its energy and power density.²¹ A battery's current and voltage determine the energy and power density, metrics that dictate the theoretical maximum performance. While total current is based on the size of the battery, voltage is an intrinsic property of the system based on the difference in the redox half reactions at the anode and cathode. The lithium reduction reaction occurs at the most reducing potential of all elements (-3.0401 V vs. NHE).²² This allows the unreduced lithium ions to act as charge balance for many other highly reductive electrochemical reactions, unlocking electrochemical cells with large voltage differences, thus, increasing the energy and power density of lithium ion based batteries.

There are many ways to fabricate both cathode and anode electrodes, but often many electrodes are made by mixing active material with conductive carbon and polymeric binder and then cast as a slurry.²³ Electrodeposition is another method used as the primary electrode fabrication technique pioneered by the Prieto group for making pure phase alloy materials for both lithium and sodium ion batteries.^{24–28}

As stated before, sodium-ion batteries work analogously to lithium-ion batteries but there are a number of important differences that have limited them from being developed to the same level as commercialization as lithium counterparts. Sodium is a larger atom and has a less reductive half reaction compared to lithium (-2.71 and -3.0401 V vs. NHE, respectively) changing some of its electrochemical properties.²² In short, the differences in chemistry affect all aspects of the battery: changes in the anode, cathode and electrolyte are each briefly discussed.

The primary commercialized anode material for lithium ion batteries, graphite, functions as an intercalation material where lithium ions fit in-between the layers of graphite during the charging of the battery.²⁹ Due to the atomic size of sodium (102 vs. 76 picometers for sodium vs.

lithium one plus ions),³⁰ sodium does not effectively sodiate graphite, meaning alternate anode materials are required.¹⁶ High capacity anode materials are heavily researched specifically in the area of alloying materials for both lithium and sodium anodes.³¹ Silicon has the highest theoretical capacity for lithiation, and like graphite, is not compatible with sodium as there is a high energy cost of inserting Na into crystalline Si.^{32,33} Other alloying elements like antimony and tin effectively lithiate and sodiate making them good systems to compare between the two alkali ions.³²

Sodium cathode materials have lower specific capacities compared to their lithium counterparts due to the higher molecular mass of sodium, with few reaching above 200 mAh/g compared to lithium cobalt oxide, which is 274 mAh/g.³⁴ Developing new cathodes is another area of ongoing research for sodium ion batteries.³⁵ Figure 1.3 shows some of the different anode and cathode materials with their approximate capacity.³⁶



Figure 1.3. Lithium and sodium, A and B, respectively, electrode materials and their gravimetric capacity vs. the voltage they react. Grey are anode materials and blue are cathode materials. Adapted from Oszajca et.al. 2014.³⁶

The process of testing new materials and optimizing batteries is often carried out using half-cell electrochemical set ups. Half cells use the respective alkali metal as the counter and pseudo-reference in a two-electrode cell. Half cells are often used due to their simplicity, as there is no need for charge balancing the cell, allowing researchers to focus on one material of interest.

Finally, the electrolyte used for sodium ion batteries is lifted directly from those used with lithium being primarily comprised of cyclic and linear carbonates to dissolve an alkaline salt.³⁷ Sodium ions has different solvation in these solvents than lithium ions. Cesce et. al. 2016 explored the difference in sodium and lithium hexafluorophosphate (PF₆) solvation in carbonate solution.³⁸ Lithium is coordinated by approximately 4 oxygens or fluorine atoms from PF₆⁻ while sodium is slightly below 6 with ~3.1 from carbonyl oxygens and ~2.5 from fluorine atoms from PF₆⁻.³⁸ The impact on battery performance from the difference in solvation shell is unclear. A fundamental scientific approach to understand the effects of the sodium electrolyte has on battery performance will remove a lot of the trial and error based approaches which were used to optimize lithium ion batteries.^{39,40}

During the operation of an alkali ion battery, the electrolyte decomposes and reduces to form the solid electrolyte interphase (SEI).⁴¹ The term was first coined by Peled ECS 1979 where, for non-aqueous batteries, alkali and alkaline earth metals are instantly covered in a layer when immersed in electrolyte.⁴² In the field it is called interphase or interface interchangeably but either term is correct. The term SEI is also applied to the passivation of anode materials or an inert electrode when battery operating potential is applied while immersed in non-aqueous electrolyte.⁴¹ The SEI should self-passivate a surface preventing further electrolyte decomposition while maintaining ionic conductivity. Thus the SEI must be electrically insulating, ionically conductive, and mechanically stable in order to function correctly in a battery.⁴¹ Extensive studies have been carried out trying to characterize the SEI using a variety of analytical techniques including X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), electron dispersion spectroscopy (EDS), X-ray diffraction (XRD), surface enhanced Raman spectroscopy (SERS), scanning tunneling microscopy (STM), and many others.⁴³⁻⁴⁶ Of these techniques, XPS is most

heavily used to study the SEI. The SEI is a mixture of organic and inorganic components that are thought to form during the operation of the battery. There are two models that describe the SEI, the mosaic and layer models. The mosaic model depicts the SEI as different sized domains of different components while the layer model consists of an inner inorganic layer and an outer organic layer.^{41,47} Neither model has been fully characterized, including definitively how the heterogeneous mixture is assembled, all components of the mixture, domain size of the components, and which aspects derive specific properties. Ultimately the true nature of the SEI is yet unknown. Both lithium and sodium ion batteries have a large irreversible capacity loss in the first cycle which is attributed to reduction of the electrolyte to form the SEI.⁴⁸ Over the course of the lifetime of the battery the SEI must passivate the surface from further electrolyte decomposition. A SEI that does not effectively passivate the anode will allow the electrolyte to continue to be consumed leading to the depletion of the alkali ion supply and the growth of an impeding layer that limits the electrode's performance. Ultimately, the SEI is a necessary part of the battery and can also be a failure mechanism if it is not functioning correctly. This dissertation focuses on learning more about the formation of the SEI in sodium ion batteries.

The SEI forms from the electrolyte via a chemical reaction but characterizing the products is not simple. The SEI is a heterogeneous thin film that forms on the anode's surface during the operation of the battery without any oxygen or water contamination. To begin to understand the SEI, one must start by controlling the electrolyte, which is the starting material in its formation reaction. Sodium salts used in the literature are primarily NaPF₆ and NaClO₄ dissolved in dimethyl, diethyl, and ethylene carbonate (DMC, DEC, and EC).^{49,50} Other carbonates such as propylene carbonate (PC) and ethylmethyl carbonate (EMC) have been studied as well but are not covered in this dissertation. There are also electrolyte additives used to improve battery performance by

changing the SEI's properties.⁵¹ Fluoroethylene carbonate (FEC) and vinylene carbonate (VC) are two of the most commonly used electrolyte additives that extent cycle lifetime of a variety of anode materials in both lithium and sodium systems.^{52–60} These additives are thought to improve the SEI by sacrificially reducing to effectively passivate the surface from further electrolyte reduction.^{61–} ⁶⁴ Identifying how FEC improves battery performance in sodium batteries is a focus of this dissertation to reveal if it is similar process to lithium batteries.

1.3. Electrochemical Society: Interface Excerpt

The following section comes from a published perspective entitled "Electrodeposition as a Powerful Tool for the Fabrication and Characterization of Next Generation Anodes for Sodium Ion Rechargeable Batteries," published with Kelly Nieto as a co-first author and Amy Prieto as corresponding author in the *Electrochemical Society: Interface*.⁶⁵ This perspective argues that electrodeposited films for sodium anode materials offer a variety of advantages from studying the intrinsic active materials sodiation pathways, creating interesting architectures, and acting as model systems for studying the SEI. The selected section for this dissertation is focused on the effect of electrolyte in sodium systems and ties together with the questions being probed in the other chapters which are outlined below.

The same electrolyte additives, FEC and VC, used in Li-ion battery systems to increase battery lifetime (shown in Figure 1.4.) are also capable of functioning in Na-ion battery systems.^{54,56} Similar to electrode materials, the sodium electrolyte has been adapted from equivalent lithium systems.^{49,50}



Figure 1.4. Adapted with permission from Everett et al. 2016. Depicted on the left are SEM images of Cu₂Sb nanowire arrays after 100 cycles with (a) 5% FEC, (b) 5% VC and 250 cycles with (c) 5% FEC, and (d) 5% VC. On the right a graph of capacity vs. cycle number for Cu₂Sb nanowire array anodes cycled in half cells between 0.10 and 1.60 V vs. Li/Li⁺ either with no additive (red), 5% FEC (blue), or 5% VC (green). The square symbols are lithiation capacity and circles are de lithiation capacity.

While the SEI has been well studied to understand the beneficial properties of electrolyte additives, there has not been a complete characterization of its composition, which limits the ability to generate design guidelines for next generation electrolytes. The SEI is a difficult system to study as it consists of a small concentration of air sensitive products deposited on an electrode surface.^{43,66} The SEI products are subject to extreme potentials and may be evolving with the charge and discharge of the battery. Furthermore, techniques to study the SEI are ex-situ and, in taking apart a battery to characterize the anode's surface, the SEI may be changed, and soluble species may wash away. X-ray photoelectron spectroscopy (XPS) is the most accessible surface sensitive technique to study SEI species, but air-free infrared spectroscopy and solid state nuclear magnetic resonance are used as well. Altogether, direct characterization of SEI species is limited by the few comprehensive in-situ techniques. The results of these different characterization tools

can be more clearly understood with electrodeposited electrodes as the data would be the result of the interaction of the electrolyte with a pure, additive free active surface.

Due to its simplicity, a half-cell design with a sodium metal pseudo-reference counter electrode is used to evaluate the anode performance of new sodium electrodes and 3D architectures. Alkali metals form a passivation layer upon immersion in electrolyte; sodium is more reactive than lithium meaning a thicker passivation layer forms on sodium.⁶⁷ The passivation layer, which does not have the same impact in lithium, affects the quality of sodium metal as a reference electrode in a half cell. Specifically, electrochemically active decomposition products cause erroneous signals in sodium ion cells.⁶⁸ The passivation of sodium metal further complicates batteries cycled in a half-cell configuration. Sodium metal soaked in battery electrolyte has been shown to cause a color change, implying a change in the bulk electrolyte, not just a passivation of the metal surface (Figure 1.5).⁶⁹



Figure 1.5. Adapted from Pfiefer et al. 2019. These are four images of sodium metal placed in battery electrolyte (a) immediately after addition in EC-DMC with NaClO₄ which is representative of the other electrolytes tested and (b) in EC-DMC NaClO₄ (c) in PC NaClO₄ and (d) in EC-DMC NaPF₆ after three days.

A color change in the electrolyte implies that the starting material for SEI formation includes unknown decomposition products. Aspects of our research are focused on understanding the role of the additive FEC in the passivation of sodium metal and how that impacts battery lifetime. To our knowledge, no complete characterization of electrolyte decomposition products has been performed. Again, this is due to a lack of specialized techniques for examining a difficult multiphase dynamic system. Nevertheless, there is a need for careful controlled experiments to understand the identity of the spontaneous reaction products and the properties they have when dissolved in the electrolyte and deposited on the surface of an electrode. The study of new electrodes may also implement alternatives to the use of sodium metal in half cells. Full cells are a clear possibility; however, sodium cathode materials are limited. Symmetric cells, which involves using a pre-sodiated anode material cycled against an unsodiated electrode, may be another alternative. Finally, a recent article by Lee et al. proposes the use of a silver ion reference electrode to help alleviate the problems the sodium counter electrode has as a pseudo reference.⁷⁰

As the understanding of the reactivity of liquid electrolytes used for sodium-ion batteries is in its infancy, the use of directly electrodeposited materials for active electrodes is an ideal platform for probing, characterizing, and then understanding libraries of liquid electrolytes and additives that could be used to significantly improve the overall performance of new materials for sodium-based batteries. What we have hopefully highlighted in this article is that while electrodeposition of electrode materials for batteries can be a useful synthetic method, it is also an enabling technology for studying the fundamental structure and properties of these materials in the absence of complications with binders, but also can be used to generate higher order architectures for batteries.

The commercialization of the lithium ion battery took twenty years.^{34,71} The ongoing climate crisis does not allow for the same timeline to commercialize sodium ion batteries as there was for lithium. This means careful experimentation geared at understand how the sodium battery system works will be required to commercialize these systems. This dissertation will be focused on understanding how the electrolyte in a sodium ion battery interacts with the anode material in

order to inform the field on important considerations when testing new sodium electrode materials. Herein, this dissertation will contain work targeted at understand how the SEI forms in sodium ion batteries using air free XPS to examine species that form on the anode surface. The anode material used to study the SEI is primarily electrodeposited Cu₂Sb, an alloy material. Electrodeposition allows for the study of SEI on a thin film of pure active material without the interference of a slurry cast electrode, which mixes active material with carbonaceous binders and additives adding additional variables that may affect SEI formation. XPS is a surface sensitive technique measuring approximately only the first 10 nm of the analyte. This surface sensitivity is due to the photoelectrons being characterized using their kinetic energy meaning only photoelectrons from the surface that do not have energy loss due to collision are measured. XPS will be discussed in more detail as a technique to study SEI in Chapter 4. The main hypothesis is that the presence of FEC in the electrolyte will show important SEI species by XPS on the surface of the anode which effect the performance of the battery. To control the SEI as much as possible while staying close to literature precedented electrolyte systems, 1M NaClO₄ 1:1:1 EC:DMC:DEC was chosen. In order to ensure FEC was the sole source of fluorine PF₆ was not largely used for experimentation.

1.4. Chapter Outline

Chapter II is designed to be a part of a larger XPS methodology manuscript to published with Dr. Leslie Kraynak and Jessica Gallawa. It depicts important considerations for using XPS to study SEI in batteries and offers a perspective the use of the technique. It focuses on the importance of determining a representative XPS spectra for a SEI created under particular conditions. This chapter explains the data processing involved in determining statistical significance of particular aspects of the XPS spectra. Often in the literature, XPS of the SEI is presented as a single spectra. My experience studying the SEI using XPS has shown that a single spectrum is frequently not representative of the species present from a particular experimental condition. Instead, multiple spectra of replicate spectra are overlaid, and an average spectrum is generated to show a more representative spectra of the species present in the SEI.

Chapter III takes sodium ion half cells and breaks down their first discharge into voltage regions where the SEI is formed. The chapter is published in the Journal of Power Sources (Gimble, N. J.; Kraynak, L. A.; Schneider, J. D.; Schulze, M. C.; Prieto, A. L. X-Ray Photoelectron Spectroscopy as a Probe for Understanding the Potential-Dependent Impact of Fluoroethylene Carbonate on the Solid Electrolyte Interface Formation in Na/Cu2Sb Batteries. *J. Power Sources* **2021**, *489*, 229171. https://doi.org/10.1016/j.jpowsour.2020.229171.) Differential capacity is used to show at which voltage SEI forming redox reactions are occurring. Batteries with and without FEC were cycled in voltage regions without electrochemistry, with electrochemistry due to SEI, and with electrochemistry due to sodiation of the Cu₂Sb active material. It was discovered that FEC greatly affects the SEI species measured with XPS at all three potential regions. Additionally, in batteries without FEC cycled in the voltage regions with little to no electrochemistry occurring, significant SEI species were observed. This result implies that important aspects of SEI formation and the impact of FEC is occurring immediately upon cycling. Furthermore, the immediate formation of the SEI became a focus of future research.

Chapter IV focuses on breaking down the sodium ion half-cell to learn more about how the SEI is formed. The second chapter seeks to understand which conditions form the initial SEI species from samples without FEC cycled in the electrochemical region with little electrochemistry occurring. It was discovered that immersing sodium metal in battery electrolyte using a scintillation vial to simulate the conditions of a half-cell resulted in a color change over time, which correlated with the formation of the previously observed SEI species. These experiments were

13

repeated using conventional half cells and the same XPS results were observed. This implies that SEI species are forming spontaneously, which has broad reaching implication for researching sodium ion batteries thus these results were condensed into a communication.

Finally, Chapter V concludes the dissertation summarizing the work presented and looks into future directions and questions that can be explored next.

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II: USING X-RAY PHOTOELECTRON SPECTROSCOPY TO STUDY THE SOLID ELECTROLYTE INTERPHASE: CONSIDERING IMPORTANT VARIABLES AND HETEROGENEITY IN SODIUM ION BATTERY SAMPLES²

2.1. Introduction

X-ray photoelectron spectroscopy (XPS) is a powerful technique for studying the surface of electrode materials in alkali ion batteries. XPS is extremely surface sensitive, mostly nondestructive, can be performed air free, and is well adapted to study the electrochemistry that occurs on surface of electrode materials. Other surface sensitive techniques include electron dispersive spectroscopy (EDS), secondary ion mass spectrometry (SIMS), and synchrotron-based X-ray techniques. EDS is an order magnitude less surface sensitive than XPS, SIMS instrumentation can be cost prohibitive and destructive, and synchrotrons X-ray techniques can also be destructive, require travel, and are system limited, making each of these techniques less viable for studying the surface of electrode materials in batteries than XPS. There is also a concern that studying batteries must be done air free, as oxygen and water will affect the results of cycled batteries or are the sodium or lithium metal electrodes.

XPS often utilizes a monochromatic X-ray source (high energy ionizing radiation usually either aluminum or magnesium K α radiation) to produce the photoelectrons and measure their kinetic energy, which can then be correlated to an element and its binding environment.¹ Binding energy of photoelectrons an element can also provide information about its chemical environment. A single wavelength energy source is important as then the binding energy is calculated from the

² This work is intended to be integrated with work by Dr. Leslie Kraynak, Jessica Gallawa, and Prof. Amy L. Prieto to be a larger X-ray photoelectron spectroscopy methodology manuscript for studying the solid electrolyte interphase in batteries.

measured kinetic energy and the work function of the instrument (ϕ), following equation 1 in the form of a gaussian peak.

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi)$$
(Eq 2.1.)

Photoelectrons must maintain their kinetic energy in order to reach the detector and be measured, meaning inelastic collisions result in photoelectrons that cannot be attributed to any element in the sample, ultimately becoming a part of the background. Thus, XPS is performed at ultra-high vacuum and is extremely surface sensitive, as only atoms on the first few nanometers of the surface can eject photoelectrons that can escape into the vacuum without experiencing an inelastic collision. This surface sensitivity makes it an ideal technique for studying and understanding the solid electrolyte interphase (SEI), a thin film that forms from the electrolyte on the anode in alkali batteries. XPS has been used heavily to study the SEI but to varying success as the SEI is complicated system to examine. ^{2–5}

Primarily, XPS can identify the elemental composition of a surface as each element has a distinct photoelectron and auger electron (a photoelectron electron ejected via a different physical process) spectrum.⁶ Alloy electrodes are commonly comprised from elements that are easily identified by XPS, that is to say, they have large relative sensitivity factors (RSF). The RSF is a normalized value of the probability for a particular photoelectron to be produced. Ultimately, the kinetic energy, and thus binding energy, of photoelectrons measured using XPS is dependent on the chemical environment of the atom. Deconvolution of peaks is dependent on the extent of overlapping binding energies from different photoelectrons, as well as peak shifting for a particular element. For transition metals, peak shifting is often an indication of oxidation state, as differentiate the chemical environment of an element based on binding energy. This is especially pronounced for

carbon, which is heavily incorporated in the SEI as the SEI is derived from the organic electrolyte. For example, the functional group of a carbon atom can be identified using binding energy position. Less polarizable nonmetals such as oxygen have smaller binding energy shifts based on their chemical environment.

Studying sodium batteries instead of lithium batteries using XPS has a few differences: lithium has a very small RSF (0.025) and in low concentrations can be missed altogether.^{7,8} Sodium is easily detected (RSF 1.685) and, as such, can be used a tool to measure how many inorganic components are present in the SEI as it is the sole cation formed in the system.^{7,8} Furthermore, sodium reactivity, as discussed throughout this dissertation, can be observed directly in certain XPS samples. Sodium plasmon loss phenomena, an event in which the photoelectron loses a specific amount of energy due to interactions with surface phonons, has been observed in work contained in this dissertation (Figure S3.8). This feature only occurs when sodium metal is present on the surface of a sample. One hypothesis for the origin of sodium metal on the anode material is that the counter pseudo reference is drifting causing sodium metal to plate onto the anode material something that has not been observed or discussed previously. This hypothesis is further discussed in Chapter III.

Although XPS is a versatile and powerful technique for studying the SEI, as with every experimental method, it does have limitations. When studying the SEI with XPS one must recall that the limit of detection for the technique is 0.1-1% concentration in the analyte. Sources of error for the technique include X-ray flux, analyzer pass energy, aperture settings, dwell time per data channel, area of sample available for analysis, and fitting procedure.⁹ Many of these error sources remain constant for a particular instrument but may need to be considered when comparing

literature data. The goal of this Chapter is to discuss and offer insights on the fitting procedure, where there can be the most variability from user to user.

Importantly, beyond XPS instrument and fitting error, there are many variables that impact the SEI. These variables that may affect the SEI include electrolyte formulation, state of charge or voltage of the cell when a measurement is made, cycle rate, voltage range, cycle number, and electrode material. Often, alloy battery electrodes are built using carbonaceous binders to make a slurry cast film, convoluting the carbon XPS. Using metal alloy electrodes as pure films to study the SEI allows carbon to come solely from the SEI as it is formed. Throughout this dissertation as many of these variables have been controlled as possible, including the use of electrodeposited active material electrodes without the convolution of binders. Despite this effort, in many different experiments, XPS spectra of the SEI from replicate samples had high variability. This heterogeneity was observed through the overlaying of multiple replicate samples in figures, then quantified in tables.

The two sections *X-ray Photoelectron Spectroscopy* and *Data Analysis* from Chapter III describe how XPS spectra is collected and then fit, taking into account as many of the previously mentioned variables as possible. This chapter will go into additional detail on this process and give specific examples that show some of the insights that can be gained by using XPS to study the SEI in sodium-ion batteries. These insights include fit peak minimalization and deconvolution, coupled peaks, plasmon loss events, and understanding what a representative spectrum is using basic statistics. Herein, we will focus on the most reliable method of fitting and accurately reporting SEI XPS data.

2.2. Fitting SEI XPS Data

Casa XPS is one of the programs used to fit high resolution XPS spectra: it is used exclusively to fit the XPS data in this dissertation. To begin to correctly understand and interpret XPS, the data must be calibrated as the binding energies shift depending on if the surface becomes charged due to continued ionization. Often, XPS spectra are calibrated to the adventitious, aliphatic carbon that occurs in every spectrum due to a combination of dust, vacuum grease, and ambient carbon. There can be variability in this calibration peak across different locations and instruments but the aliphatic carbon can be used effectively for self-consistent calibration.¹⁰

The first step in fitting XPS data is selecting a baseline type. A Shirley type baseline is the most accurate type of baseline and used most prevalently in literature.^{11,12} Background noise increases at higher binding energies especially after a photoelectron peak and baseline selection must account for this. The Shirley baseline bends upward to match how the baseline shifts.

Fitting XPS is a source of considerable consideration as one must avoid overfitting the data. Briefly, Gaussian-Lorentzian peaks can be inputted and manipulated until a fit matches the raw data. Each peak *must* represent a chemical environment that is present in the sample. The Ockham's Razor type approached used in this dissertation limits the number of fit peaks to the minimum number of known chemical environments that could possibly be present in the SEI samples while accurately fit the raw data. Overfitting of the data, that is to say adding in peaks that either do not reflect the sample being measured or do not significantly improve the fit of the data, can lead to incorrect interpretations of data, and should certainly be avoided.



Figure 2.1. Oxygen 1s and antimony 3d XPS spectra from published data in Chapter III. Black line is the raw data, red is the peak envelope. Oxygen 1s fit peaks are green and yellow representing perchlorate oxygen and oxygen on carbon. Antimony 3d fit are two sets of two peaks (5/2 and 3/2) in representing antimony oxide and antimony metal as light blue and blue. Finally, the sodium auger KLL peak is in grey.

Fitting oxygen in an SEI sample is a good example for this Ockham's Razor methodology and involves many useful fitting techniques. The oxygen 1s photoelectron is highly convoluted in a Cu₂Sb sodium-ion battery system as between 525 and 545 eV the oxygen 1s, antimony 3d, and sodium KLL auger photoelectron peaks are all present, as shown in Figure 2.1. When fitting such a convoluted spectrum it can be simplest to start with p, d, or f photoelectrons as they generate coupled peaks.^{7,13,14} In this example, the antimony 3d coupled peaks are known to have a 3d 5/2 peak that is exactly 1.5 times larger than the 3/2 peak, to have the same full width half max peak shape, and to be located exactly 9.34 eV apart.^{7,15} The specifics of these correlations for other p, d, and f electrons are all element dependent and can be found in the XPS handbook along with any exceptions.⁷ Experience fitting different SEI systems and elements will help teach which peaks are finicky and which peaks are consistent. In this case, there are two antimony environments, metal, and oxide. Antimony metal 5/2 and 3/2 are at 527.9 and 537.2 eV, respectively, while the antimony oxide peaks are at 530.6 and 539.9 eV. Of these four peaks the antimony oxide 5/2 at 530.6 and antimony metal 3/2 at 537.2 eV are convoluted by other photoelectron peaks. Due to the strict coupling of the 3d peaks, the exact peak shape is known based on the other, non-convoluted partner peak, simplifying the data, and allowing for fewer assumptions. Thus, for the antimony oxide 5/2 example, the extra signal, beyond that attributable to the 3/2, at 531.4 eV must come from oxygen 1s signal. Based on the location of this peak, the oxygen signal is attributable to oxygen bonded to carbon (hydroxides and carbonates appear between 530.5-532 eV).⁷ In the other convoluted peak, antimony metal 3/2 at 537.2 eV, which also is defined exactly based on its partner peak, the remaining signal is attributed to a sodium KLL auger electron centered at approximately 537 eV. The final peak used to fit this oxygen XPS data is the unconvoluted signal at 533.5 eV, representative of perchlorate oxygen originating from residual salt. This example on how a highresolution oxygen spectrum was fit demonstrates the importance of knowing fundamental information on how photoelectrons are generated, and an initial understanding of the different components which are possible in the sample in order to deconvolute multiple overlapping peaks. With this background knowledge it is much easier to accurately deconvolute a complex spectrum with several overlapping signals.

Careful fitting of carbon XPS data has been pivotal for gathering meaningful data and understanding of carbon speciation in the SEI. The carbon that comprises the SEI has different levels of oxidation with aliphatic carbon, singly oxygenated carbon, carboxyl carbon, and carbonate carbon all having been observed in different SEI samples in Chapters III and IV. Additionally, when conducting XPS on sodium metal samples, a reduced carbon species has been
observed (283.6 eV), which could indicate the presence of a carbide species. Adding further complexity to fitting of carbon spectrum, the field has some discrepancy on carbon peak assignment of the highest binding energy carbon peak (~291 eV, present in Figure 2.2), which is often attributed to fluorinated carbon.¹⁶ Literature results rely on the attribution of this peak to fluorinated carbon when commenting on the role of fluoroethylene carbonate (FEC) and LiPF₆ on SEI formation, and thus their effect on battery performance.^{17–19} In this dissertation fluorine is carefully controlled and no corresponding fluorine peak is observed, meaning there is no fluorinated carbon present. However, the ~291 eV carbon peak is present, indicating that in the samples studied herein this fit peak is assigned to carbonate carbon. However, the fluorinated carbon hypothesis cannot be eliminated as easily in spectra taken on materials that do contain fluorine. If one is looking to attribute the ~291 eV carbon peak to fluorinated carbon the corresponding fluorine peak must also be collected and fitted to validate this hypothesis.

In all cases, if a peak is attributed to a particular chemical environment that involves bonding to another element, that other element must corroborate the initial peak assignment. In the previous oxygen example, if perchlorate chlorine had not been present then the perchlorate oxygen assignment would have been inaccurate.



Figure 2.2. Carbon 1s XPS spectra of pristine 1:1:8 NaCMC: SuperP: antimony slurry electrode (top left), NaCMC slurry electrode (top middle), SuperP slurry electrode (top right), and cycled sodium ion batteries of the full slurry electrode (bottom).

Although deconvoluting XPS data is possible in many cases, XPS is not a suitable technique in every situation. In complex slurry-based systems the complexity of the sample does not lend itself to successful and *meaningful* interpretation. Work done with Kelly Nieto shows some of the perils of deconvoluting carbon XPS when studying slurry electrodes.²⁰ Figure 2.2 depicts carbon 1s XPS spectra from a pristine 1:1:8 sodium carboxymethylcellulose (NaCMC) : SuperP : antimony slurry cast electrode (Figure 2.2, top left). SuperP is a commercially available conductive carbon black powder. Deconvoluting the carbon environments is possible in this uncycled, unreacted electrode by studying each component used individually. Three fit carbon peaks can be seen in the spectrum from a slurry of just NaCMC (Figure 2.2, top middle), corresponding to carboxyl, singly oxygenated, and adventitious aliphatic carbon peaks. The final peak is shown as sp2 hybridized carbon, as seen in the spectra of only the SuperP slurry (Figure 2.2, top right), slightly below 285 eV. Concerningly, the pristine electrode already contains many

of the environments expected to be observed as SEI species making it difficult to delineate SEI species from components of the electrode. Once the film is cycled (Figure 2.2, bottom), further complications arise as to whether the carbon species being observed are solely from the SEI over the slurry additives or from a combination. Furthermore, adventitious carbon signal is very difficult to separate from the slurry, making calibration a significant challenge in these systems. If self-consistent calibration is not achieved, then no accurate discussion of the XPS data can be made. As such, it is nearly impossible to use XPS to accurately and carefully make conclusions about SEI on slurry-based electrodes.



2.3. Accurate Reporting of Reproducibility

Figure 2.3. Three overlaid carbon XPS spectra from batteries cycled between 0.05 and 0.6V vs. Na/Na⁺ a part of work presented in Chapter III. Two spectra from two spots on the same battery while the third spectrum is from a separate replicate battery.

Ensuring representative XPS spectra of a SEI sample are studied is crucial to making accurate conclusions and interpretations of data. Figure 2.3 shows three overlaid carbon 1s XPS

spectra, two from different spots on the same battery and one from a separate replicate experiment. This data shows clearly that heterogeneity is present in SEI formed under these conditions both across replicate samples as well as across the surface of a single sample. Often in the literature XPS data collected on SEI is represented as a single spectrum, which may result in misleading conclusions on SEI properties and components. It is often unclear if researchers have run multiple samples, multiple spots across one sample, or if they simply took one scan. As such, explicit descriptions of what was measured and how variable the data is are needed to accurately make statements about the results and convey the true scientific meaning.

When attempting to correlate a specific difference in the XPS spectra attributable to a changed variable in the experiment, and thus in SEI formation, that difference in XPS should be quantitatively determined to be statistically meaningful. Replicate samples, both across electrode surface and produced from a separate experiment, must be examined with XPS, and characterized to determine the relative error for each fit peak in order to determine if an observed difference in chemical environment concentration, or SEI species is meaningful.



Figure 2.4. Carbon 1s XPS spectra of batteries assembled under three different experimental conditions. This data is a part of work presented in Chapter IV.

Figure 2.4 depicts three sets of XPS spectra from three different sets of experiments found in Chapter IV. The highlighted carbon environment, singly oxygenated carbon, clearly looks to be bigger for the graph on the left compared to the middle and right graph. But, in order to make this qualitative observation quantitatively meaningful, the standard deviation of the average peak position and peak area are required. In this dissertation, each experimental condition was repeated three times and XPS spectra were generated from three different locations for a total of nine spectra being collected representative of each set of conditions. The average peak position and standard deviation for the highlighted fit peak in question are 286.66 ± 0.06 , 286.7 ± 0.1 , and 286.60 ± 0.10 eV (Figure 2.4, left to right, full data set Table S3.1), where all three values are within the standard deviation error of each other, meaning they are the same chemical species assigned as singly oxygenated carbon. The average peak concentration for this fit environment is 13 ± 2 , 7 ± 2 , and $9 \pm 1\%$ concentration (Figure 2.4, left to right, full data set Table S3.3), demonstrating definitively that singly oxygenated carbon fit peak for graph on the left is statistically different than those for the middle and right graphs. The statistical difference is smaller than the visual difference further highlighting the importance of statistical analysis. Because the percent concentrations are statistically different, meaningful interpretation of this data is possible.

The graphs in Figure 2.4 attempt to visualize this statistical analysis by showing all of the individual spectra in grey with a black spectrum that is an average of all spectra measured. The closer the grey lines are to the black line, the less variability there is for that particular set of experiments. This is the type of XPS figure that is presented throughout this dissertation and statistical relevance is the basis for any conclusion about SEI composition.

2.4. Conclusions

While there are a multitude of variables that affect SEI formation, certain steps can be taken in order to ensure conclusions are based on correctly fit, reproducible XPS data. Through understanding the possible components that may be present in the SEI, conclusions can be made by measuring other elements or supplemental analytical techniques. Replicates are paramount when studying the SEI with XPS as sufficient data is necessary for accurate conclusions. Shown here, both creating representative spectrum and making accurate distinctions in XPS can only be done through sufficient replicate data. XPS is a powerful tool to study the SEI, however, it must be done in a way that is scientifically rigorous.

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III: X-RAY PHOTOELECTRON SPECTROSCOPY AS A PROBE FOR UNDERSTANDING THE POTENTIAL-DEPENDENT IMPACT OF FLUOROETHYLENE CARBONATE IMPACT OF FLUOROETHYLENE CARBONATE ON THE SOLID ELECTROLYTE INTERFACE FORMATION IN Na/Cu₂Sb BATTERIES³

3.1. Overview

The solid electrolyte interface (SEI) forms from electrolyte decomposition during the initial discharge of half-cell batteries and is affected by the presence of electrolyte additives. Breaking down the initial discharge into stages, defined by voltage cut offs, can help discover the role of additives in SEI growth. In this study, X-Ray Photoelectron Spectroscopy (XPS) is used to analyze the SEI formed on electrodeposited, binder free Cu₂Sb thin films in sodium ion half-cell batteries. The presence of fluoro-ethylene carbonate (FEC), an electrolyte additive known to enhance battery lifetime, has a significant effect on the carbon 1s XPS spectra. The concentration of oxygenated carbon environments is dramatically decreased when FEC is added to the system. These environments were present in samples without FEC before significant electrochemistry was observed, potentially displaying the reactivity of sodium metal with conventional carbonate electrolytes to form the initial components of the SEI before the battery is cycled. The differences observed when FEC is added are likely the chemical environments of the SEI that have the

³ This manuscript is published in the *Journal of Power Sources* with Nathan J. Gimble, Leslie A. Kraynak, Jacob D. Schneider, Maxwell C. Schulze, and Amy L. Prieto (*J. Power Sources* **2021** 289 229171.). Nathan J. Gimble carried out all experimental procedures, characterization, and manuscript preparation. Leslie A. Kraynak assisted with conceptualization, methodology, and editing the manuscript. Jacob D. Schneider assisted with the creation of air-free XPS sampling and manuscript editing. Maxwell C. Schulze assisted with data processing, figure configuration through writing software and manuscript editing. Amy L. Prieto assisted with project administration, funding acquisition, and manuscript editing.

dramatic effect on battery performance. Interestingly, these results suggest that the critical aspects of SEI formation are determined before the active material is sodiated, with FEC playing an integral role.

3.2. Introduction

Energy storage is a critically important area of research due to the emergence of the lithium-ion battery (LIB), which has led to the proliferation of portable electronic devices and fully electric vehicles. High capacity batteries have broader applications with the threat of climate change requiring the development of renewable energy sources in parallel with energy storage technologies.¹ There are concerns about the availability of lithium in terms of the scaling of battery technology to large-scale grid storage applications. Sodium ion batteries (NIB) cost 30% less compared to LIBs and sodium is three orders of magnitude more abundant in the earth's crust, making it a target for large-scale energy storage applications.²

Current commercial LIBs and developing NIBs use an organic liquid electrolyte to facilitate the diffusion of the working ion between the electrodes.³ The electrochemical window of these electrolytes is within the operating voltage of the battery, degrading the electrolyte to pseudo-passivate the anode surface forming the solid electrolyte interface (SEI).^{3–5} The electrolyte solvent used ubiquitously in battery literature and commercial battery construction is comprised of different organic carbonates including ethylene carbonate (EC) and propylene carbonate (PC) usually mixed with dimethyl carbonate (DMC) and diethyl carbonate (DEC).^{3,6–9} There are numerous variations on this theme adding to the complexity of the literature as each electrolyte component contributes to the SEI's composition and properties.^{6,10} The supporting electrolyte also plays a role in SEI formation adding another layer of variability. Lithium hexafluorophosphate

(LiPF₆) is the most common supporting electrolyte; lithium perchlorate (LiClO₄), lithium bis(trifluoromethane) sulfonimide (LiTFSI), lithium bis(oxalate)borate (LiBOB), as well as more toxic salts are present in the literature as well.^{6,10,11} These same anions and electrolyte solvents have been used to study analogous sodium ion battery systems.^{12–14}

The SEI is extremely important in battery performance, requiring specific properties: it should be electronically insulating to prevent additional electrochemical reduction of the electrolyte, ionically conductive to allow the supporting ions to travel through to the electrode surface, and mechanically stable as to not expose new surfaces for additional SEI formation.^{15–19} There is a large, sometimes as great as 60%, irreversible capacity loss between the first and second cycle of a LIB or NIB battery, attributed to SEI formation.²⁰ Additionally, the SEI is a failure mechanism as uncontrolled SEI growth exacerbates pulverization of the anode or completely impedes ionic mobility.^{5,21,22} During SEI formation, the properties described are self-selected for by the conditions in which the SEI is grown. The SEI functions as a solid electrolyte thus studying its components has applications beyond batteries in the progress of fast ionic conducting materials.

Specific small molecule additives have been used widely in battery literature to improve battery performance.^{6,10,23,24} Fluoro-ethylene carbonate (FEC), one such additive, has been widely used to extend battery lifetime.^{25–29} Previous modeling and experimental research on FEC found it to act sacrificially forming preliminary SEI components to control growth.^{30–38} One hypothesis explaining the beneficial properties of FEC is that it assists with ion conduction in the SEI by creating nano-scale deposits of LiF, or NaF in the sodium analog, while creating an electronically insulating surface.²⁵ However, this hypothesis is not known conclusively. The same idea applies to the utilization of LiPF₆, which also adds fluorine to the system.^{11,39} While trends are emerging regarding the role of additives, further characterization of the SEI species on the surface is required

to link structure to properties. Additives used in Li-ion systems have been used in Na-ion batteries showing improved battery performance, which is unprecedented.^{12–14} Further research is needed to learn more about how the small additives such as FEC form the SEI in a sodium system to guide optimization and development.

In order to further improve liquid electrolytes, especially for Na-ion batteries, a thorough understanding of what components are present on the anode surface at a particular voltage in the cycling process, especially with regards to the effect of additives is crucial.⁴⁰ Without exploring this issue more, it is difficult to understand how the SEI is functioning. Through experimentation in a lithium system, the SEI is thought to contain organic and inorganic components that may or may not be formed in layers.^{41,42} Reaction schemes and models have been proposed to describe electrolyte decomposition, however, the products shown in these reactions do not provide a complete understanding of the SEI's effect on battery performance as it is difficult to relate these results back to the desired SEI properties.^{16,30,31,43–45} The majority of studies performed on the SEI use a lithium ion system, which cannot always be directly applied to sodium. Lithium and sodium have different reactivities, alloying pathways, and migration properties; understanding how these differences apply to SEI formation will lead to important information about ionic conductivity, electrolyte selection and reactivity.^{46,47} Recent studies have been exploring the difference in sodium and lithium reactivity revealing sodium metal to be spontaneously reactive with carbonate electrolytes making it a lower quality reference and counter electrode for half-cell battery experiments.^{48–54} The role of FEC in this reactivity is particularly interesting as recent work from Dugas et al. 2016 proposes that FEC forms a protective layer on the surface of Na metal that assists with battery cycling.⁴⁹ Understanding this reactivity and what role it plays in the growth of the SEI

on pure phase active material will be critical for improving and optimizing NIB systems for researching novel electrode materials.

Measuring and understanding how, as well as if, the SEI forms at different points during battery cycling is a difficult task. Differential capacity analysis takes the differential of the total charge passed as a function of voltage. Peaks in differential capacity are a sign of an electrochemical event at a particular voltage and may be used to observe when SEI is forming on the working electrode. However, because the SEI forms under anerobic conditions as a thin film on the surface of the anode material, it is not easy to determine what has formed. Many analytical techniques have been used to characterize the SEI however, no single technique is capable of elucidating its true nature as once again it is difficult to correlate results to the desired SEI properties.^{19,55} X-ray photoelectron spectroscopy (XPS) is the most applicable technique used to study SEI as it is surface sensitive and will be the primary tool used in this study.^{15,19} XPS is minimally invasive however, remaining cognizant of how utilizing a specific analytical technique is changing the SEI is important.⁵⁶ Because many of the applicable techniques are performed *ex*situ, the operation of disassembling the battery in and of itself may be changing the SEI in some capacity.⁵⁷ In XPS interpretation, no conclusion will be made that reaches beyond the capability of the technique.

The previous work studying SEI is inconsistent as variables tested such as lithium vs. sodium, electrolyte composition, cycle rate, voltage ranges, and electrode material are often not taken into account.^{15,18,19} Additionally, the heterogeneity of SEI species is not heavily researched, an important note as anode materials and substrate properties may play a role in SEI growth. Fabrication of anode materials commonly utilizes carbon binders, convoluting whether the carbon signal is from the binders or the SEI in the carbon XPS and introducing reactive surface sites for

SEI growth. Additionally, the presence of binders fundamentally changes the chemical properties of the surface which can change how SEI grows.⁵⁸ The SEI forms from the electrolyte primarily during the initial charge, or discharge in the case of half cells, and it is likely at this stage that the crucial aspects of the SEI are forming that affect battery lifetime. Preceding studies have tried to break apart the initial cycle based on Li/Na alloying rather than potentials corresponding to SEI formation leading to results that do not represent how the SEI is growing.^{59–63}

In this study, XPS is used to analyze electrodeposited Cu_2Sb as an anode material assembled in a sodium ion battery half-cell. The anode Cu₂Sb was chosen as it is a promising anode material due to it cyclability, high electrical and thermal conductivity, and resistance to pulverization.^{64,65} Electrodeposited Cu₂Sb provides a unique system to study how SEI forms on pure high density alloys without the presence of binders. We study conventional electrolytes with and without FEC to elucidate the additive's role in SEI growth. To examine SEI growth, the initial discharge of the half-cells was broken into regions based upon features in the differential capacity to discover a correlation between electrochemical events and XPS elemental environments. This hypothesis leads to understanding at what point crucial SEI components are being formed and focus on the particular chemical reactions occurring can begin. Sodium perchlorate was the supporting electrolyte assuring that FEC is the sole fluorine source in the system. The additive FEC was found to have a significant effect on the carbon XPS signals suppressing the singly oxygenated and carbonate carbon environments from the very beginning of battery cycling. This signifies that FEC plays an immediate role in which components are present on the surface of the anode material. This leads to the understanding of how these components contribute to the desired SEI properties.

3.3. Experimental

3.3.1. Electrodeposition of the Cu₂Sb Electrode

The Cu₂Sb anode material being studied was synthesized via electrodeposition. The electrodeposition solution was comprised of 400 mM citric acid and 25 mM antimony (III) oxide (Sb₂O₃, nano powder, 99.9+% Aldrich) which was left to dissolve with the help of mechanical stirring for twelve hours at 60° C. When the solution was clear, 80 mM copper (II) nitrate hemipentahydrate (Cu (NO₃)₂, 99.9+% Aldrich) was added turning it to a vibrant light blue. This solution was then titrated dropwise, with continued mechanical stirring, to pH 6 with saturated KOH, causing the color to shift to a darker royal blue. All water used in the electrodeposition solution was Millipore water (18 M Ω). Copper substrates were prepared by electropolishing for fifteen seconds in a solution of 2:1 H₃PO₄: H₂O to remove the oxide layer on the copper surface. The substrate was thoroughly washed with Millipore water, rinsed with 200 proof ethanol, and air dried. A custom electrodeposition cell (Figure S3.1) was used where the substrate was the working electrode with a stainless-steel mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A Gamry Reference 3000 potentiostat was used to apply a constant voltage of -1.05 V vs. SCE for 10 minutes to form the purple-grey pure phase copper antimonide anode material, which was used to study SEI formation. This copper antimonide synthesis was developed and discussed in a previous report.⁶⁶

3.3.2. Battery Assembly and Cycling

Half-cell batteries were assembled in an argon glove box ($O_2 < 1$ ppm) using Swagelok PFA straight tube fittings with a half-inch bored center. Half-inch punches from Cu₂Sb films, Na metal, two polypropylene (PP) separator punches, glass microfiber filter paper (Whatman), 200 mL of electrolyte solution, and stainless-steel mesh were assembled in the configuration shown in Figure S3.2. The electrolyte solution comprised of 1 M sodium perchlorate (NaClO₄, Sigma Aldrich ACS Reagent) supporting electrolyte dissolved in 1:1:1 portions of ethylene carbonate (EC, recrystallized), dimethyl carbonate (DMC, Anhydrous Sigma Aldrich \geq 99%), and diethyl carbonate (DEC, Sigma Aldrich Anhydrous 99%) by weight, as well as for certain experiments, 5% fluoroethylene carbonate (FEC, Sigma Aldrich \geq 99%) by volume. The half cells were cycled on an Arbin BT2000 series battery tester under constant current conditions. Preliminary half cells were subjected to 5 discharge and charge cycles between 2 and 0.02V vs. Na/Na⁺ at a rate of C/50. Subsequent potential region experiments were cycled between 2 and 1.75V, 1.75 and 0.6V, and finally 0.6 and 0.02V vs. Na/Na⁺ for the high (HPR), middle (MPR), and low (LPR) potential regions respectively. Each battery potential region cycling experiment was repeated four times with Cu₂Sb punches from four different electrodeposited films. These regions were used for samples with and without FEC. Potential regions experiments were cycled twenty times across their respective voltages. Twenty cycles is sufficient time at these potential regions to develop any electrochemical products on the anode surface for analysis. Cycled cells were disassembled in the argon glovebox and the Cu₂Sb films were washed with 300 µL of DMC before transfer to the Xray photoelectron spectrometer (XPS) using a sealed air-free transfer holder. Each potential region had many replicate samples to get an idea of heterogeneity in each sample and reproducibility.

3.3.3. X-ray Photoelectron Spectroscopy

Samples were transferred air-free from the argon glove box to the PE-5800 series Multi-Technique ESCA system intro chamber where 30-minute-high resolution (HRES) scans were performed on two center spots and one edge spot for each anode. Examining multiple spots will explore heterogeneity across a single SEI surface. Additionally, each experiment was repeated four

times using different electrodeposited films to explore the reproducibility of SEI formation. An Al Ka monochromatic source operating at 350.0 W is used for all XPS experiments. High resolution scans were used to analyze all possible elements: carbon 1s, oxygen 1s, chlorine 2p (Figure S3.5), fluorine 1s, and sodium 1s. For the high potential region, copper 2p and antimony 3d were also detected. A self-consistent fitting method using CasaXPS software was employed to analyze the results. All high-resolution spectra were calibrated to the aliphatic carbon peak at 285 eV. This calibration method uses the assumption that lowest binding energy carbon peak is aliphatic carbon in the sample and is a common XPS fitting practice.^{67,68} Other peaks in the system matched appropriately making the calibration self-consistent. That being said, comparing peak position to other work may not be appropriate as a different instrument and battery assembly conditions may result in a different aliphatic carbon calibration. The fitting process utilizes a Shirley background to account for when the background shifts at higher binding energies. Peaks were fit using an Ockham's Razor-style approach looking to minimize the number of binding environments that were used to match the data. All fitted peaks are gaussian and for a given element the full width half max (FWHM) is constrained to not exceed 1.5 times any other peak as it is unlikely that environments from the same element have highly variable FWHM. Photoelectrons with split peaks such as the chlorine 2p and antimony 3d are constrained to each other completely following the known information about each split.⁶⁹ Finally, the percent composition of each element and chemical environments was calculated by Casa XPS using relative sensitivity factors (RSF) values from Physical Electronics.⁶⁹

3.3.4. Data Analysis

Each element's raw XPS spectra from replicate samples were overlaid and an average spectrum was created to show heterogeneity. Creating an average spectrum required first subtracting the variable baseline counts of each spectrum due to inconsistent chamber pressure. A Python code was written that subtracted every Y electron counts/second value by the smallest measured number in a particular scan, which was used as the baseline value. After the transformation, overlaid spectra could be compared visually, and an average spectrum could be created. The code created the average spectra by binning each X-axis binding energy value to the nearest 0.1 eV then averaging each corresponding Y-value across every replicate scan. This creates an average spectrum for each element in each potential region in an attempt to account for heterogeneity. The Python code used in the baseline subtraction and spectra averaging can be found in the supporting information. The development of an average spectrum allows for trends in each region to be observed more clearly. Quantification data derived from fit peaks, which was unaffected by the background subtraction as it was already based upon peak area above the background, was used to understand the differences in SEI samples and compare replicate samples. The peak position and environment concentration for each fitted peak in replicate samples was averaged giving a standard deviation, effectively representing the amount of heterogeneity for that environment in a given set of samples. An example of the Python code used is in the Figure S3.3.

3.4. Results and Discussion

In order to explore the electrochemistry of the initial discharge for this system, a battery with and without FEC was cycled at a C/50 rate.



Figure 3.1. Differential capacity plot of the first discharge for sodium ion batteries with a A) 1 M NaClO₄ 1:1:1 EC: DMC: DEC and B) + 5% FEC. Highlighted potential regions are shown in blue, orange, and green for the HPR, MPR, and LPR respectively where batteries were cycled 20 times.

Differential capacity plots of the batteries cycled at the slow rate (C/50) were used to formulate three potential regions in the initial discharge of the half-cell battery as shown in Figure 3.1. The first region between 2 and 1.75 V vs. Na/Na⁺, and finally, herein defined as the high potential region (HPR), is where very little if any electrochemistry is occurring. The middle potential region between 1.75 and 0.6 V vs. Na/Na⁺ (MPR) is where electrolyte decomposition electrochemistry is occurring but no reductive sodiation of Cu₂Sb. Both experiments with and without FEC have peaks centered at 1.25 V vs. Na/Na⁺ contained in this region. Sodiation electrochemistry is contained in the low potential region (LPR) between 0.6 and 0.02 V vs. Na/Na⁺, the onset of the sodiation event is observed occurring at 0.5 V vs. Na/Na⁺. There was no significant difference in these voltage regions when FEC was added, thus, to keep this variable consistent, the selected regions were used for both sets of experiments. XPS can be used to explore any correlation between the electrochemistry observed in differential capacity to the different species on the surface of Cu₂Sb.



Figure 3.2. Differential capacity plots for replicate battery samples cycled with 1 M NaClO₄ 1:1:1 EC: DMC: DEC in the A) HPR, B) MPR, and C) LPR, then batteries with 5% FEC vol. cycled in the D) HPR, E) MPR, and F) LPR.

Differential capacity plots for HPR samples, MPR samples and LPR samples cycled with 1:1:1 EC: DMC: DEC electrolyte solvent with and without FEC are shown in Figure 3.2. Generally, the electrochemistry observed in replicate experiments for each potential region were similar with the most significant differences occurring in the MPR. However, these differences are minute, as the Ah/V values are very small. The differences observed are likely due to variable surface roughness, local Cu-Sb ratios and amorphous oxides present.⁷⁰ The Y-axis of the HPR differential capacity plots are an order of magnitude smaller than the middle and low potential regions confirming little to no electrochemistry is occurring in the selected voltage region. The onset of electrolyte reduction occurring in the MPR as seen as larger differential capacity values are approximately two times larger for samples without FEC. This is counterintuitive as FEC is thought to act sacrificially during the initial SEI growth.^{30–37} The LPR differential capacity plots reflect this phenomenon as well showing more capacity passed in samples without FEC before the reductive sodiation of Cu₂Sb. Lower charge passed suggests that the presence of FEC impedes the amount of electrolyte reduction in the initial discharge potentially resulting in a longer battery lifetime. Monitoring differential capacity ensured that each battery had similar electrochemical events occurring on the Cu₂Sb surface matching the original goal of identifying SEI growth based on electrochemistry observed.



Figure 3.3. Overlaid Carbon 1s XPS spectra of all spots from replicate batteries cycled with 1 M NaClO₄ 1:1:1 EC: DMC: DEC in A) HPR, B) MPR, C) LPR without FEC and D) HPR, E) MPR, and F) LPR with FEC. Aliphatic carbon, singly oxygenated carbon, carboxyl carbon, and carbonate carbon environments are labeled at their approximate binding energy for each collection of spectra. Each overlaid spectra have an average spectrum as a darker black line.



Figure 3.4. Average percent concentration of carbon environments from fit XPS spectra for replicate experiments cycled with (above) and without (below) FEC in the HPR (2-1.75 V), MPR (1.75-0.6 V), and LPR (0.6-0.02 V vs. Na/Na⁺). Aliphatic carbon concentration is shown in blue, singly oxygenated carbon in red, carboxyl carbon in green, and carbonate carbon in yellow.

High resolution carbon 1s XPS spectra from Cu₂Sb samples cycled in the different potential regions with and without FEC are shown in Figure 3.3. The quantification of fitted peaks are presented in Figure 3.4, numerical quantification values for this plot are present in Table S3.1. In addition, the average peak position for each fitted peak is tabulated in the SI. It should be noted that the standard deviation of the average peak position ranged from 0.02-0.6 eV. This implies that in replicate samples, heterogeneity is based not on the components changing but rather their relative abundances. There are four carbon environments of various levels of oxidation. The first fitted peak is aliphatic carbon at 285 eV, which is present in all spectra collected. Aliphatic carbon is present in the majority of XPS as most surfaces exposed to atmosphere gather it on the surface. This makes it difficult to determine how much C-C and C-H environments are coming from SEI and how much is adventitious, especially since adventitious carbon is not controlled.⁶⁷ In

experiments cycled in the MPR and LPR without FEC, the aliphatic peak has significant error likely due to variable adventitious carbon. Singly oxygenated carbon, also present in every sample, appears at 286.8 eV. At 288.6 eV is the carboxyl carbon environment appearing in a consistent, small concentration across each sample with slightly higher average concentrations in FEC-containing experiments. Finally, the carbonate environment appears at 290 eV without FEC and 291 eV with FEC. The carbonate environment is not present in the HPR FEC containing batteries but appears in the MPR and persists in the LPR. XPS spectra are taken under ultra-high vacuum, thus these carbon environments are representative of SEI species adhered onto the surface and not any residual electrolyte.

The striking difference in these sets of carbon XPS spectra is the significantly larger singly oxygenated and carbonate carbon environment in the HPR samples without FEC compared to samples with FEC. The concentration, as calculated from the fitting of peak areas, of these peaks is nearly *double* when FEC is not present. Since these carbon environments have appeared on the Cu₂Sb anode surface in the HPR where the electrode is only slightly polarized, they form before significant electrochemistry has occurred. Measuring SEI species in the HPR contradicts the original hypothesis that electrochemistry observed in the differential capacity plots could be correlated to SEI growth. Instead, the presence of these carbon environments implies that in the HPR, the SEI is forming spontaneously on the active material before any current is applied. Previous research into spontaneous reactivity of sodium metal have only examined the effect on the sodium counter electrode or comparing half-cells to full cells but not on the anode material.⁵¹ Ultimately, the singly oxygenated and carbonate environments observed in the HPR suggest that sodium metal reactivity affects SEI formation in half-cells before electrochemistry has occurred.

environments associated with electrolyte reduction (adventitious carbon is still present) on the surface. This suggests that FEC may be preventing sodium metal from reacting with the electrolyte and depositing reaction products onto the active material's surface as initial SEI components which is different from what is hypothesized to occur in lithium systems. Exploring this reactivity and its effect on SEI growth is the focus of ongoing research.

When more reductive current is passed in the MPR, a carbonate carbon peak at 291 eV emerges as well as an increase in the singly oxygenated carbon peak at 286.8 eV for samples with FEC. This means surface SEI features grow as a result of electrochemistry observed in differential capacity when FEC is added to the electrolyte. This phenomenon follows the original hypothesis. The presence of FEC is playing a role in how the SEI is formed during the initial stages of battery assembly and experimentation. By studying SEI as a function of voltage the effect of FEC as perhaps a sacrificial additive can be observed more clearly. Ultimately, there is still further research needed to learn about how FEC reacts with sodium metal.

Closer examination of the newly emerged carbonate peak in the FEC MPR spectra reveals that the peak is centered around 291 eV, not 290 eV, where it is found without FEC. The disparity in binding energy of the carbonate environment between the two sets of experiments is interesting as both 290 and 291 eV fit in the binding energy envelope of carbonate carbon.⁶⁹ It is unlikely the 291 eV peak in FEC experiments is fluorinated carbon, as it is commonly characterized to be, because there is no analogous fluorine peak appeared in the same XPS scan (Figure S3.4), only sodium fluoride. Thus, the difference in carbonate peak position is believed to be due to the ionic carbonate environment potentially having a slightly higher binding energy than a covalent carbonate environment. Ionic carbonates form in higher concentrations when FEC is present while covalent carbonate form more commonly in samples without FEC.⁷¹

Reviewing the LPR results, there are no new carbon environments observed, however, the singly oxygenated peak concentration, calculated from peak area, has more error in replicate samples compared to the more oxidizing potential regions. Increased error is likely due to heterogeneities becoming exaggerated as the electrolyte is exposed to more reducing potentials. Regardless, the presence of FEC suppresses the growth of singly oxygenated and carbonate containing components before electrochemistry has begun. Thus, the organic constituents that result in the singly oxygenated and carbonate signal in the HPR carbon XPS spectra could be a detriment to battery lifetime and can be prevented with the presence of FEC.



Figure 3.5. Overlaid oxygen 1s XPS spectra of all spots from replicate batteries cycled with 1 M NaClO₄ 1:1:1 EC: DMC: DEC in A) HPR, B) MPR, C) LPR without FEC and D) HPR, E) MPR, and F) LPR with FEC. Perchlorate oxygen, oxygen bonded to carbon, antimony and antimony oxide $3d_{5/2}$ and $3d_{3/2}$ environments are labeled at their approximate binding energy for each collection of spectra. Each overlaid spectra have an average spectrum as a darker black line.



Figure 3.6. Average percent concentration of oxygen environments from fit XPS spectra for replicate experiments cycled with (above) and without (below) FEC in the HPR (2-1.75 V), MPR (1.75-0.6 V), and LPR (0.6-0.02 V vs. Na/Na⁺). Oxygenated carbon concentration is shown in blue, perchlorate oxygen in red.

Oxygen 1s XPS spectra with and without FEC are shown in Figure 3.5 and the corresponding quantification data reported in Figure 3.6 (numerical values for average concentration and peak position present in Table S3.2). Antimony 3d photoelectron peaks appear at similar binding energies to the oxygen 1s photoelectron. Antimony has a large RSF value and, thus, is easily detected with XPS. Being a part of the electrode, if antimony is observed, the SEI is less than 10 nm thick as 10 nm is the approximate distance photoelectrons can penetrate through and be observed.⁶⁹ The antimony 3d peaks appear in the HPR and MPR FEC experiments, as well as all three spots on one sample cycled in the HPR without FEC. The presence of antimony and antimony oxide 3d_{5/2} and 3d_{3/2} peaks show that the SEI in these experiments is less than 10 nm thick. The relative thickness of the samples that do not include antimony supports the results

observed in the carbon spectra where samples without FEC as well as batteries cycled in the LPR have more material present in the SEI and are thus thicker.

Oxygen environments attributed to the SEI observed during these experiments include perchlorate oxygen at about 533 eV and oxygen on carbon, including any C-O and C=O species, at 531.5 eV.^{69,72} Oxygen on carbon peaks are larger when FEC is not present matching carbon XPS data, while perchlorate concentrations are constant given error, the only exception being HPR FEC samples having less perchlorate oxygen than oxygen on carbon. Studying the oxygen XPS spectra in this system does not reveal the same detail as the carbon spectra since oxygen bonded to carbon does not differentiate based upon the organic functional group in which it is contained. One final detail about the oxygen 1s spectra is when the antimony peak is obscured by the SEI, like in the no FEC MPR samples and all LPR samples, there is a small peak is present around 537 eV. This peak is the KL₁L₂₃ sodium auger peak appearing due to increased sodium concentrations in the SEI.⁶⁹ The presence of this peak further complicates fitting clear oxygen environments and drawing conclusions from the different types of oxygen that are present in the samples.

Analogous to the LPR carbon XPS spectra, replicate LPR oxygen XPS spectra were more heterogeneous than samples cycled at more oxidizing potentials. Particularly, the concentration of perchlorate oxygen fluctuated immensely in replicate LPR experiments. Additionally, samples without FEC exhibit a new oxygen peak at 530 eV conceivably attributed to Na₂O or NaOH.⁶⁹ The sodium auger peak in no FEC LPR is aligned correctly showing that the peaks are calibrated correctly. These heterogeneous signals suggest that the conditions occurring on the surface when the battery is cycled in the LPR are inconsistent. The source of this inconsistency may be related to previous research showing sodium metal to be a poor reference electrode.^{48,49,52–54,73} If the reference electrode is changed, the measured voltage at the working electrode will be different

than the potential it is actually experiencing. Thus, it is possible that differences in the passivation of the sodium metal pseudo-reference electrode from replicate samples compounded to the point observed in the XPS, through the different potentials felt on replicate surfaces.



Figure 3.7. Overlaid sodium 1s XPS spectra of all spots from replicate batteries cycled with 1 M NaClO₄ 1:1:1 EC: DMC: DEC in A) HPR, B) MPR, C) LPR without FEC and D) HPR, E) MPR, and F) LPR with FEC. Sodium cation, sodium fluoride, and sodium metal plasmon loss environments are labeled at their approximate binding energy for each collection of spectra. Each overlaid spectra have an average spectrum as a darker black line.



Figure 3.8. Average percent concentration of sodium cation environments from fit XPS spectra for replicate experiments cycled with (above) and without (below) FEC in the HPR (2-1.75 V), MPR (1.75-0.6 V), and LPR (0.6-0.02 V vs. Na/Na⁺). The primary sodium cation concentration is shown in blue, sodium fluoride in red. Note, sodium fluoride was present in LPR samples with FEC, but heterogeneity prevented an accurate quantification.

Deciphering qualitative information from the sodium 1s XPS spectra shown in Figure 3.7 can be difficult as many sodium environments overlap in binding energy.⁶⁹ The general trend from the quantification data in Figure 3.8 (numerical values and average peak position present in Table S3.3) reveals that on average samples without FEC contained roughly 50% higher sodium concentrations than their FEC counterparts for a given potential region. SEI reactions are likely irreversible, meaning there are significant faradaic efficiency repercussions for supporting electrolyte consumption. Sodium concentrations also increase as batteries are cycled at more reducing potentials, reflecting the increase in the KL₁L₂₃ sodium auger peak observed in the oxygen 1s spectra. Sodium plays an important role in the SEI makeup as it is the only cation in the system. This means any anion formed from the electrolyte couples with sodium, and, if insoluble,

precipitates onto the surface as part of the SEI. The primary peak at 1072 eV is likely comprised of Na₂CO₃, NaClO₄, and other larger carbon anions such as NaROCO.⁶⁹ The primary sodium peak at 1072 eV does not move in position across every sample collected. Additionally, samples containing FEC have a shoulder at higher binding energies centered at 1073.5 eV due to the presence of NaF that is known to have a different binding energy than other sodium salts.⁶⁹ Examining the Na 1s XPS spectra of FEC containing batteries cycled in the LPR reveals certain scans show the shoulder peak to be more intense than the primary peak. This level of heterogeneity lead to quantification results that could not be compared directly and were thus omitted. The reason for this heterogeneity is likely the same for the differences observed in the oxygen XPS spectra, relating to inconsistent passivation of the sodium counter electrode inducing irreproducible potentials on the surface of Cu₂Sb when cycled in LPR conditions.

The LPR Na spectra without FEC displayed different features on certain scans which is not present in any HPR or MPR experiments. Complimentary peaks at 1075 eV and 1070 eV appear together and were not quantified. These peaks are thought to be due to plasmon loss of sodium metal, which has not been heavily documented in literature due to the extremely reactive surface that is quickly oxidized to form sodium salts. This phenomenon would not have been observed without the capability to perform XPS experiments air-free. Plasmon loss is not observed on pristine sodium metal surface as prepared for half-cell experiments (Figure S3.6). However, this feature has been observed before supporting the conclusion that sodium metal as shown from the plasmon feature in certain LPR samples supports the hypothesis that the potential on the surface is not accurately between 0.6 and 0.02 V vs. Na/Na⁺ (an expanded plot of the sodium metal plasmon effect as well as the auger peaks are shown in Figure S3.7). The reaction of sodium metal

with the electrolyte passivated the sodium counter electrode to the extent that instead of holding a 0.02 V vs Na/Na⁺, the working electrode felt a voltage below the 0 V vs Na/Na⁺ plating the observed sodium metal on the surface. The previous research on sodium metal half cells has shown sodium to be a non-ideal pseudo-reference and the presence of plasmon peak may be an artifact of sodium counter electrode being overly altered.^{48,49,52,53,73} An alternative hypothesis for this observation is that the SEI in the sample with no FEC in the LPR became too thick, thereby developing a significant overpotential resulting in sodium metal plating. However, the cycling program did not allow for the voltage to go below 0 V vs. Na/Na⁺, and we observe no signature of Na plating in the dQ/dV plots. Despite these potentially variable conditions, the presence of FEC leads to the formation of NaF, which may also play a role in how FEC expands battery lifetime although XPS is incapable of explaining why. Nevertheless, XPS has shown significantly differing results based upon the presence of FEC and has revealed the extent to which the initial discharge affects SEI formation in sodium half-cell batteries on electrodeposited Cu₂Sb.

3.5. Conclusion

XPS was used to study the SEI formed on electrodeposited Cu₂Sb half-cell anodes in a sodium system using conventional electrolytes with and without the presence of the FEC small molecule additive, previously observed to dramatically extend battery lifetime. Specifically, the initial discharge of these batteries was broken into potential regions based on the electrochemistry occurring in differential capacity plots in order to probe the SEI formation. Initially, it was thought that electrochemistry observed in differential capacity could be correlated to chemical environments in XPS. However, in samples cycled without FEC singly oxygenated and carbonate carbon appeared in the HPR where little to no electrochemistry was observed in the corresponding differential capacity plot contradicting the hypothesis. Alternatively, in samples containing FEC a

carbonate peak appeared in the MPR samples after peaks were observed in the differential capacity supporting the hypothesis. Additionally, studying replicate experiments revealed how the heterogeneity manifested itself at more reducing potentials. Ultimately, the system is more complicated than scope of the original hypothesis as it is likely the sodium metal pseudo-reference counter electrode that is responsible for the different results observed. The HPR samples without FEC show significant SEI formation without considerable electrochemistry occurring, suggesting spontaneous electrolyte reactivity had occurred. Additionally, the complicating effect of the sodium counter electrode was observed at more reducing potentials as its unreliability as a reference electrode resulted in electroplated sodium metal on the working electrode. Determining the extent of the effect of this reactivity is the focus of ongoing research especially in relation to FEC. Additionally, examination of any electrolyte reactivity should be explored in full cell battery experiments. These results show that FEC is able to passivate sodium metal differently than the conventional electrolytes, which has significant impact on how the SEI grows on the anode material and the function of the additive in sodium ion systems. This report has highlighted the importance for understanding electrolyte-surface interaction during the initial discharge of a halfcell experiment and demonstrated the importance of FEC in that first interaction. Furthermore, the results have broad implications in the development of new sodium ion battery materials and electrolytes, the creation of a fast ion conductors, or a sodium metal anode battery system.

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IV: SPONTANEOUS SOLID ELECTROLYTE INTERPHASE FORMATION IN UNCYCLED SODIUM HALF-CELL: USING X-RAY PHOTOELECTRON SPECTROSCOPY TO EXPLORE THE PRE-PASSIVATE OF SODIUM METAL BY FLUOROETHYLENE CARBONATE BEFORE APPLIED ELECTROCHEMSITRY⁴

4.1 Overview

Developing new sodium technology, particularly batteries, often utilizes a half-cell two electrode setup involving a sodium metal counter electrode. Herein, utilizing a series of controlled experiments, it is shown that the reaction between sodium metal and a conventional carbonate electrolyte results in a detrimental solid electrolyte interphase (SEI) that forms spontaneously on the working electrode of a half-cell. This result is important for the field as the SEI is known failure mechanism for batteries. Furthermore, the role of the small molecule additive fluoroethylene carbonate (FEC) is revealed to pre-passivate sodium metal preventing further SEI forming reactions. Developing and improving electrolytes for different sodium systems will depend upon understanding how the SEI forms and the effect of additives like FEC.

4.2 Introduction

Sodium offers an important alternative to lithium for large scale applications in batteries and capacitors due to its natural abundance.^{1–3} Many aspects of sodium systems have been adapted from analogous lithium systems, however there are important chemical differences that make a

⁴ This chapter has been submitted to *RSC: Sustainability and Fuels* for peer review. Nathan J. Gimble carried out all experimentation, characterization, and manuscript preparation. Amy L. Prieto assisted with project administration, funding acquisition, and manuscript editing.

direct substitution of sodium for lithium challenging. For example, the difference in ionic radius between the two alkali metal ions means that graphite, the successfully commercialized intercalation anode material for lithium-ion batteries, is incompatible with sodium. Hence, alternative anodes for sodium batteries are required.⁴

Additionally, reports in the literature indicate that common liquid electrolytes are more reactive when in contact with sodium as compared to lithium.^{5,6} Liquid electrolytes commonly include linear and cyclic organic carbonates to dissolve the supporting alkali salt.⁷ These electrolytes react with lithium or sodium to passivate their surfaces, but the sodium products have a higher solubility, which may help explain the observed enhanced reactivity because the surfaces cant passivate as completely.^{8–10} Despite the many issues caused by the higher reactivity of sodium metal, few studies have examined the effect of sodium reactivity and the working electrode, the material being tested, in a half-cell.^{11–14} If sodium metal reactivity affects the material being tested then true device performance cannot be realized. To effectively improve battery performance all aspects and interactions in the system must be understood. Specifically, in a half-cell, the questions of how the sodium metal reactivity affects the solid electrolyte interface (SEI) formation remains unanswered.

Though the SEI effects battery performance, its formation is still not well understood.^{8,15,16} Previously, we examined reductive electrochemical liquid electrolyte decomposition into the SEI as a function of applied potential on Cu₂Sb in sodium metal half-cells using X-ray photoelectron spectroscopy (XPS).¹⁷ Our results showed that fluoroethylene carbonate (FEC), a small molecule additive that has been widely studied because it improves cycle lifetime in both sodium and lithium batteries, has a significant impact on the SEI species observed at different voltages during the initial discharge of half-cells, where the SEI is thought to form.¹⁷ The additive FEC is thought to improve cycle lifetime by acting sacrificially, decomposing onto the anode's surface, to build a SEI that benefits the cell.^{18–21} One hypothesis, proposed by Dugas et. al., suggests that FEC may form a stable inner layer and an evolving outer layer on sodium metal with cycling, though no conclusion on the true nature of how FEC passivates and affects sodium metal has been reached.²²

Notably in our previous work, we show that without FEC, there is a significant quantity of SEI species on the surface of Cu₂Sb at potentials where little charge had passed.¹⁷ Subsequently, we hypothesized, and show herein, that the base carbonate electrolyte reacts with sodium metal spontaneously and the products of this reaction diffuse across the half-cell to deposit onto Cu₂Sb as initial SEI species. Furthermore, we hypothesize and again show that FEC works differently than previously thought in the literature: instead of reducing onto the anode during cycling, FEC prevents the previously mentioned initial spontaneous SEI formation through pre- passivating sodium metal prior to any applied electrochemistry. Numerous control experiments are utilized below to test if the SEI is forming spontaneously and to explore the function of FEC in sodium-ion half-cells. Our data indicated that initial SEI species form on the working electrode of a sodium half-cell with no applied potential. The importance of FEC is further highlighted as it can prevent the formation of many of the initial SEI species. These results demonstrate the importance of understanding SEI formation and how electrolyte additives such as FEC impact this process, which will be crucial for effectively developing sodium technologies.

4.3 Results and Discussion

To understand how SEI products are forming, three electrolyte conditions were explored using different experimental methods. Electrolyte condition **1** is 1 M sodium perchlorate (NaClO₄) in 1:1:1 ethylene carbonate (EC): dimethyl carbonate (DMC): diethyl carbonate (DEC), a common simple electrolyte system. Condition 2 is the base electrolyte 1 with 5% FEC added. Finally, condition 3 is sodium metal soaked in pure FEC for 48 hours before use with condition 1.



Figure 4.1. Molecular level diagrams of the three electrolyte conditions (1, 2, and 3) in half-cells are depicted in columns 1, 2, and 3, respectively. Column 3 begins in the first row showing the 48-hour pre-soak of sodium metal in FEC. The second row represents the initial immersion of sodium metal under each electrolyte condition. The third row shows each system days later. The fourth row has photographs of sodium soaked in each electrolyte condition (A, B, and C) after five days.

Shapes used are: Base electrolyte (1 M NaClO₄ EC: DMC: DEC) as yellow circles, base electrolyte decomposition products as orange squares, FEC as blue triangles, and FEC passivation products as green upside-down triangles.

Over several days of soaking sodium metal in condition 1, a cloudy yellow color change occurred, similar to the changes seen by Pfeifer et. al. (an electrolyte system without FEC) (Figure 4.1A) (before images shown in Figure S4.1).⁶ The color change is likely due to reaction products dissolving into the electrolyte. Condition 2, with 5% FEC added, resulted in an electrolyte solution that remained clear and exhibited no color change (Figure 4.1B). Condition 3 also results in no color change suggesting, for these soaking experiments, the passivation of sodium by FEC may have the same effect as FEC in solution. Characterization of the source of the color change by NMR proved difficult due to the low concentration of reaction products (Figure S4.3). Meticulous air-free separation techniques would be required to accurately identify these products. To explore the conditions of the color change, sodium metal was immersed in individual liquid carbonates with and without different supporting salts (Figure S4.2). The salt NaClO₄ is used as the supporting electrolyte to ensure that FEC is the sole source of fluorine, although other salts caused a more intense color change (Figure S4.2). A crucial result was that without a salt, no color change is observed. However, the sodium metal surface exhibited different species measured using XPS even when the solution remains colorless (Figure S4.4), indicating that although there is no color change detected by eye, there is still some surface reactivity and presence of salt may impact reaction product solubility.

Sodium metal reacts with the electrolyte causing a color change likely due to products that can redissolve in a process facilitated by the presence of a supporting salt. To test the effect on working electrodes, half-cell batteries were assembled using electrolyte conditions 1, 2, and 3, then left to rest in the glove box, uncycled. To ensure reaction products could form and, according to our hypothesis, migrate across the cell, half-cells were left for 72 hours. After disassembly, the surface of the working electrode and any initial SEI products could then by analyzed with air free XPS.²³ Following our previous work, electrodeposited Cu₂Sb anode material was used so SEI species can be observed without interference from binders or additives.^{17,24–26} For the interested reader, more information on XPS fitting and presentation can be found in our previous publications.^{17,27} XPS data of all corresponding sodium counter electrodes is present and discussed in the supplemental information (Table S4.1, Figure S4.6, and Figure S4.7).



Figure 4.2. Overlay of XPS spectra of all spots on replicate uncycled Cu_2Sb/Na battery samples. Black lines represent an average spectrum. The carbon 1s (A, D, G), oxygen 1s and antimony 3d (B, E, H) and sodium 1s (C, F, I) are presented. The electrolyte systems in the uncycled batteries are 1 (A, B, C), 2 (D, E, F), and 3 (G, H, I).

A qualitative examination each set of XPS experiments of uncycled Cu₂Sb/Na half-cell batteries reveals that the profile of each XPS spectra for condition 2 is similar to 3, which are both different from condition 1 (Figure 4.2). This supports the hypothesis that the SEI is forming spontaneously and the pre-passivation of sodium metal with FEC exhibits similar properties to having FEC in solution. Quantitative results for average peak position and peak concentration are tabulated in the supporting information (Table S1). Average peak position is extremely consistent, meaning the same environments are present in replicate experiments. The fit peak concentration error is larger, indicating there is heterogeneity in the amount of initial SEI species. Examining the carbon 1s XPS quantitatively (Figure 4.2A, D, G and Table S4.1.), the fit peak area of the singly oxygenated carbon environment at ~286.6 eV is two times larger in condition 1 compared to 2 and 3, an indication of the differing amounts of SEI species. The highest binding energy peak at 290.1 eV in battery samples is usually attributed to carbonate or fluorinated carbon.^{28,29} For all conditions it is carbonate carbon (appearing between 289 and 291.5 eV), not fluorinated carbon, as there is no fluorine in **1** and in the other two systems the fluorine is attributed to NaF (Figure S4.5).³⁰ Samples with and without FEC have the carbonate peak at 290.1eV, but without FEC (1) the peak is again roughly about two times larger, while under condition 2 the peak is just above the background. As with singly oxygenated carbon, this difference indicates the increased concentration of SEI species forming spontaneously without the presence of FEC.

The highest binding energy in the **3** samples is at 288.55 eV, which is the same with in error as **2** samples at 288.6 eV, while the third peak in **1** samples is different at 288.3 eV indicating different carboxylate species which appear between 288-289.6 eV.³⁰ The concentration of this CO_2 environment is larger under conditions **2** and **3** compared to **1**. Presoaking sodium in FEC, (**3**), has similar effects on the carbon environments as when FEC is a part of the electrolyte, (**2**), supporting

the hypothesis that FEC is benefiting the cell through passivation of sodium metal. The carbon environments in the sample without FEC (1) can be related to the stoichiometry of the SEI species. For example, the singly oxygenated carbon and carbonate species have a 2.5:1 ratio, meaning molecules with that ratio of functional groups may be included in the SEI such as sodium diethylene di-carbonate, a potentially detrimental SEI product identified in other systems.^{31–33} This data, in conjunction with additional control experiments, may help to identify the initial SEI species.

The oxygen 1s photoelectron appears at the same binding energy as antimony 3d (Figure 4.2B, E, and H). Due to the XPS detection depth of ~10 nm the presence of antimony and copper from the Cu₂Sb substrate is an indicator of SEI thickness (Figure S4.5). Without FEC (1), antimony peaks are barely above the background while antimony and antimony oxide concentration are ~4% with FEC (2) an ~5% with FEC presoaked (3). The SEI from condition 1 is thick enough to obscure the substrate in an uncycled battery clearly showing that SEI is forming in a higher quantity than under conditions 2 and 3. Oxygen is a complicated element to differentiate via XPS due to multiple chemical environments occurring at similar binding energies, thus the minimum number of peaks were assigned. Condition 1 had more perchlorate chlorine (Figure S4.5) and therefore the larger perchlorate oxygen peak at ~533 eV compared to 2 and 3. The remaining second oxygen environment was fit to oxygen on carbon at ~531 eV. Finally, a sodium auger KLL peak is fit at ~536 eV.

Like oxygen, sodium has small binding energy shifts for different chemical environments. For these experiments one sodium environment was fit, representing all potential sodium cations at ~1072 eV (Figure 4.2C, F, and I). The concentration of sodium in each half-cell for **1** is $12 \pm 2\%$, **2** is $7 \pm 1\%$, while **3** is $8 \pm 4\%$, within error of **1** and **2**. This result supports the other XPS data, suggesting more SEI species are deposited onto the surface of Cu_2Sb without FEC (1), while the surface of the FEC (2) and presoaked (3) systems are similar.



Figure 4.3. Electrochemical impedance spectroscopy Nyquist spectra, without any fit, of Cu₂Sb/Na half-cell batteries in A) **1** (orange), B) **2** (blue), and C) **3** (green). The dark line in each plot is the half-cell after assembly, intermediate line is one week after assembly, and the light line is two weeks after assembly. Overlayed D) is each EIS spectrum after two weeks.

Finally, Cu₂Sb/Na half-cells were assembled using the same electrolyte conditions **1**, **2**, and **3**. Electrochemical impedance spectroscopy (EIS) was collected after assembly, then collected again after both one week and two weeks to observe how the systems changed over time while no voltage is applied. Analogous to the XPS spectra, qualitatively, the impedance spectra of samples with electrolytes **2** and **3** are similar to each other, while **1** is different. This supports the hypothesis about the role of FEC in initial SEI formation as the reaction products on the surface of sodium metal in pretreated samples (**3**) resembles the impedance of a cell containing FEC in the electrolyte

(2). The samples without FEC (1) show an increase in solution impedance over time, which can be correlated with the chemical reaction that induced the color change highlighted in Figure 4.1A, as well as the SEI components measured using XPS (essentially, more SEI is formed, which has higher impedance than a well-passivated electrode surface).

Lifetime battery performance of half-cells in each electrolyte condition 1, 2, and 3 are compared (Figure 4.4). These experiments utilized an antimony carbon nanotube anode material instead of Cu₂Sb, as it was able to obtain longer cycle lifetime.³⁴ The battery with electrolyte 1 exhibits poor cycle life while 2 and 3 have more stable lifetimes. However, the cycle lifetime of 2 is still greater than 3. This may be due to the importance of SEI repair through available FEC in solution.³⁵ This lifetime experiment further supports the hypothesis that important performance benefits of FEC occur through its pre-passivation of sodium metal rather than decomposing onto the surface of the anode material in half-cell sodium batteries.



Figure 4.4. Cycle lifetime plots of Sb-CNT/Na half-cells with, left to right, 1 (orange), 2 (blue), 3 (green).

4.4. Conclusions

Sodium ion batteries and other sodium technologies are increasingly important as alternatives to lithium. Many emerging sodium technologies are tested using half-cell set ups using sodium metal as a counter electrode. While previous work has demonstrated that sodium metal counter electrodes are more reactive than their lithium metal counterpart, no work has been conducted examining the effect of sodium's heightened reactivity on the working electrode.^{5,6,13,22} Using uncycled sodium half-cells, SEI species are observed to form spontaneously on the working electrode, impacting its performance and supporting our first hypothesis. We show that the passivation layer of sodium metal by FEC alone is capable of preventing the SEI species from forming. This supported our second hypothesis that the benefits of FEC occur through its own passivation reaction with sodium metal, not its reduction on the anode during cycling. These results are an important step in understanding the interactions occurring in a sodium battery and provide valuable insights for testing new sodium materials and developing sodium technology.

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V: SUMMARY AND FUTURE DIRECTIONS

This dissertation focuses on identifying how the solid electrolyte interphase (SEI) forms in sodium-ion batteries. Chapter I motivates sodium-ion batteries as a sustainable alternative to lithium-ion batteries based on global distribution, price, and abundance. The chapter continues by introducing the SEI as an important failure mechanism that has been addressed using electrolyte additives in lithium-ion batteries. Interestingly, these same additives are used in sodium systems meaning additional fundamental understanding is required to optimize and innovate electrolyte additives for a sodium system. This chapter includes an excerpt from the previously published perspective (Gimble, N. J.; Nieto, K.; Prieto, A. L. Electrodeposition as a Powerful Tool for the Fabrication and Characterization of Next-Generation Anodes for Sodium Ion Rechargeable Batteries. Electrochem. Interface 2021. 30 (1).Soc. 59-63. https://doi.org/10.1149/2.F09211IF/XML.). This excerpt helps illustrate that pure phase electrodeposited anodes can be used as a model system to study the SEI.

Chapter II is to be used as part of a larger X-ray photoelectron spectroscopy (XPS) methodology paper focused on using the technique to study the SEI. This methodology paper will be co-written with Leslie Kraynak, Jessica Gallawa, and Amy Prieto. The focus of this chapter is to highlight the problems with heterogeneity, as well as the way to counter it, in the SEI as measured with XPS. Primarily, representative spectra are generated for the SEI. The SEI can be heterogeneous across a single sample as well as replicate samples making it important to create accurate representative XPS spectra. Additionally, the chapter overviews some common pitfalls in XPS fitting and interpretation.

Chapter III uses electrochemical experiments on half-cell sodium batteries to understand the formation of the SEI. Specifically, differential capacity analysis was used to identify at what voltage electrochemical reductions were occurring that contribute to SEI formation. By cycling batteries in specific voltage regions, SEI species built up in these regions could then be characterized using XPS. Furthermore, the influence of the small molecule electrolyte additive fluoroethylene carbonate (FEC) is explored both in the electrochemistry in the differential capacity and in direct characterization by XPS. It was found that FEC had a dramatic effect on the SEI species measured in each voltage region. FEC lowered the concentration of singly oxygenated and carbonate carbon in all three voltage regions. An electrochemical peak in differential capacity was correlated with the emergence of a carbonate environment in samples with FEC. Without FEC, even in the voltage region where little to no electrochemistry was observed, there were a large amount of SEI species measured.

Chapter IV expanded upon what was learned in Chapter III by looking more into the SEI species measured in samples without FEC. Batteries were assembled and left uncycled before disassembly and subsequent analysis by XPS. It was observed that without FEC, during the 72 hours the battery was left to sit without any applied potential, SEI had spontaneously formed on the anode's surface. To understand FEC's effect on this process, its presence in solution was tested in addition to its effect as a passivation layer on sodium metal. Soaking sodium metal in FEC can build up a passivation layer on the surface of sodium metal. Then that passivated sodium can be used in battery assembly where the electrolyte does not contain FEC. These experiments tested if FEC's passivation of sodium metal was how it improved battery performance. It was hypothesized that sodium metal reacted with the electrolyte to make initial SEI species that can diffuse across the cell and deposit onto the working electrode. FEC was subsequently hypothesized to prevent

this process through its own passivation of sodium metal. Both batteries with FEC in solution and batteries where the sodium metal counter electrode was soaked in FEC prior to assembly did not have spontaneous SEI formation. These results are important for developing a fundamental understanding of how the SEI forms in sodium ion batteries and testing new materials using a half-cell where sodium metal is involved.

There are multiple future directions that build on the work presented in this dissertation. A clear next step is to characterize the organic and inorganic structures and the concentration of each organic and inorganic species in the initial SEI. Ideally, this will lead to the development of balanced reaction stoichiometry for the different chemical reactions that form the SEI. Learning more about the organic structures of species present in the SEI will draw valuable structurefunction property relationships that can be correlated with battery performance. In this dissertation little reaction stoichiometry was proposed however, the reaction between sodium metal and the electrolyte is likely radical based.^{1–3} The radical based initiation of these reactions may result in various ring-opening polymerization pathways creating various oligomers. Determining the identity and chain length of these oligomers as well as how they interact with other components will be crucial for understanding the properties of the SEI. However, the electrolytes tested herein have four or five different components, meaning the radical based reaction schemes would spread into a web of different pathways and a variety of products. Additionally, any of the possible product that contains a negative charge will bond with a sodium ion. These inorganic or larger organic salts have different solubility chemistries between sodium and lithium. The color changes observed in sodium metal soaking experiments is likely related to this difference in solubility of any sodium organic or inorganic salts formed from these radical initiated reactions. Determining the concentration of each species present and the domain size can help identify which components

of the SEI are contributing to which properties. In addition, the organization of the different components may be an important consideration as well. Ultimately, just the identity and concentration of the various components formed would be difficult to determine due to the constraints of the system let alone identifying the domain size and organization. Specifically, the low concentration of SEI products, the variety of products present, and air sensitivity would make a separation and subsequent characterization difficult.

Attempts to identify products by NMR were difficult as the signal is dominated by the base electrolyte instead of the potential products (Figure S4.3). I tried an air-free distillation of a solution that had changed color where the glassware was assembled in the glovebox, however, the liquid that boiled off was clear and was pure starting electrolyte by NMR. The leftover salt was colored like the color change but could not be identified as anything but NaPF₆, which was a part of the starting solution that had the color change. Further work toward characterization of the source of the color change observed is needed, but this is a significant challenge to the field as a whole. Despite the difficulty of a full characterization, this dissertation provides valuable fundamental understanding of the difference between sodium and lithium batteries that will have widespread application.

Foremost, we have shown that having FEC in the electrolyte is crucial for understanding the true performance of a new material. Testing new sodium anodes and cathodes with a half-cell was demonstrated to be convoluted by the presence of sodium metal. Understanding the passivation of sodium metal by FEC is key for developing new sodium electrodes. Additionally, this data will assist with the discovery of new electrolyte additives that improve upon the observed function of FEC. In line with our other hypotheses, it could be critical that the products of FEC passivation on sodium metal, in addition to having beneficial SEI properties, have a lower solubility. A lower solubility may account for the passivation layer's ability to prevent other reactions from occurring by remaining intact. However, as stated earlier, thorough characterization of the products formed by FEC on sodium metal will be critical for the identification of the most important properties. Using just one molecule as a starting material instead of a full electrolyte, exploring the reaction pathways of FEC reduction by sodium metal is a good direction to target specific molecules that may be forming, research that has only just begun.^{4,5} Then, testing the properties of the proposed products will help reveal how FEC is functioning and inform on desired SEI properties. New electrolyte additives that either decompose to form more stable products or the design of effective coatings that contain desired properties can be developed and optimized to balance the higher solubility of sodium salts involved in sodium batteries.

A different future project would be to test the effect of vinylene carbonate (VC), another electrolyte additive shown to improve battery performance in both lithium and sodium batteries.^{6–} ⁹ Showing if VC is capable of the same effects as FEC would help support or disprove the hypothesis about FEC sodium metal passivation being the way FEC provides it's benefit in sodium batteries. Outside this dissertation I have done several experiments with VC that make it particularly interesting to study further. Upon immersion of sodium metal in only VC without a salt there is color change over time to a golden color (Figure S4.2). Repeating this experiment with VC as a 5% additive in base electrolyte with and without salt would be a good starting point to understand if there are any differences in product solubility or other properties between FEC and VC. However, if VC experiments have different results it does not necessarily mean the FEC hypotheses are wrong, simply that FEC and VC may function differently.

Electrolyte formulation has been heavily explored for a variety of lithium and battery systems.^{10–12} My experience with optimization revealed a few interesting considerations.

Electrolyte viscosity is an important property as some of the popular high concentration electrolytes are highly viscous, lowering ionic conductivity, and, in my experience, required a non-carbonate-based solvent to create a functional battery. Testing ionic liquids also revealed different issues as they did not wet the separator and required a glass separator as the sole separator. Exploring the anion lithium salt provided the most interesting results. Between, LiPF₆, LiFSI, LiBOB, LiClO₄, and LiDFOB, LiDFOB was the most promising.^{13,14} Using LiDFOB in combination with varied concentrations of EC, EMC, and VC the battery lifetime was improved.

Another direction for future research is the examination of SEI formation on more varied electrode substrates. The hypothesis supported by the experiments in this dissertation that the SEI forms spontaneously in sodium half-cells would suggest the substrate plays very little role in SEI formation. However, during the operation of the battery the surface properties of the substrate should affect how the electrolyte decomposes onto its surface. Thus, further exploration of the substrate may involve some combination of the two processes and is important for further understanding SEI formation. The compound SnSb, another promising electrodeposited alloy anode material, is a good first system to explore.¹⁵ In SnSb both elements sodiate compared to just Sb in Cu₂Sb. Studying the SEI that forms on SnSb will test many of the hypotheses in this dissertation. Furthermore, changing other electrode properties such as conductivity could reveal more about the role of substrate in SEI formation. Both Cu₂Sb and Cu are conductive metallic materials with Cu being an inactive electrode, mean that it will not sodiate. Cu electrodes were used for a variety of experiments (Figure S3.10, S3.11, and S3.12). Sb is a fully active semimetal material and was tested briefly (Figure S3.9). Testing insulating electrodes that are active and inactive such as phosphorous and glass, respectively, could further reveal the role of substrate in SEI formation.

The work described herein studying the SEI formation has additional applications. Computationally modeling sodium electrolyte and SEI formation is a different direction toward a fundamental understanding of a sodium battery.^{16,17} The development of new models will need to include considerations from the results of this dissertation, particularly the difference in solubility of SEI species formed on sodium metal compared to lithium. Looking toward other systems, particularly a sodium metal battery, many of the results from this dissertation apply toward the development of a sodium metal anode. Furthermore, for multivalent batteries, such as magnesium, calcium, or aluminum, fundamental understanding of the different element chemistry is needed to develop these various battery technologies. The attention to detail exhibited throughout this dissertation can act as a guide for new research studying the SEI formation in new battery systems as well as improve the SEI in sodium-ion batteries.

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APPENDIX I: SUPPORTING INFORMATION FOR CHAPER III: X-RAY PHOTOELECTRON SPECTROSCOPY AS A PROBE FOR UNDERSTANDING THE POTENTIAL-DEPENDENT IMPACT OF FLUOROETHYLENE CARBONATE IMPACT OF FLUOROETHYLENE CARBONATE ON THE SOLID ELECTROLYTE INTERFACE FORMATION IN Na/Cu₂Sb BATTERIES



Figure S3.1. Custom electrodeposition cell seals the copper substrate working electrode in contact with the electrodeposition solution in a controlled area. The stainless-steel mesh sits in the electrodeposition providing excess surface area, while the SCE reference electrode sits in the tiny hole in the stainless-steel mesh, close to the working electrode.



Figure S3.2. Graphic showing half-cell battery assembly. A stainless-steel anode bolt, sodium metal anode, PPE-glass microfiber filter paper-PPE/electrolyte separator/electrolyte, Cu₂Sb cathode, stainless steel mesh cathode collector, spring, and copper cathode bolt were used in half-cell assembly



Figure S3.3. Plots of discharge capacity in blue and charge capacity in black vs. cycle number for batteries with A) B) C) 1M NaClO4 1:1:1 EC: DMC: DEC D) E) F) +5% vol. FEC cycled in the A) D) HPR, B) E) MPR, and C) F) LPR.

This data shows that effectively all the capacity, and thus electrochemical SEI growth, of the potential region experiments occurs during the first discharge. The subsequent cycles simply allow the system to come to equilibrium. The order of magnitude for the capacity matches the discussion about the same topic for Figure 3.2. Additionally, the amount of variability in these plots matches the amount of variability from differential capacity shown in Figure 3.2.

Figure S3.4.

file1 = 'Excel file name and location' file2 = "

#extra wide range of binding energies data is within
BEmin = 275
BEmax = 302
alldata = pd.DataFrame(index=(np.arange(BEmin,BEmax,0.1).round(1)))

locations=[#Structured as [.xlsx datafile, sheet number (or name), columns to pull from, rows to skip]

```
[file1, 1, 'G,J', 3],
[file1, 1, 'K,N', 6],
[file1, 1, 'O,R', 3],
[file1, 1, 'S,V', 16],
[file1, 1, 'W,Z', 13],
[file1, 1, 'AA,AD', 15],
[file1, 1, 'AE,AH', 6],
[file1, 1, 'AE,AH', 6],
[file1, 1, 'AI,AL', 5],
[file1, 1, 'AM,AP', 7],
[file1, 1, 'AQ,AT', 13],
[file1, 1, 'AU,AX', 10],
[file1, 1, 'AY,BB', 16],
```

1

```
for num, param in enumerate(locations):
  data = read excel(param[0], #call data from excel
             sheet_name=param[1],
             names = ['BE', 'CPS'+str(num)],
             pusecols = param[2],
             skiprows=param[3])
  data = data.dropna() #remove none numbers
  data['CPS'+str(num)] -= (data['CPS'+str(num)].min()) #background subtraction
  plt.plot(data['BE'],data['CPS'+str(num)], color='gray', linewidth=0.5) #plot raw data
  data2 = data.set_index(round(data['BE'],1)) #round x-values to 0.1
  data2 = data2.drop('BE',axis=1)
  alldata = pd.concat([alldata,data2], axis=1, join='inner') #confine to one x axis
alldata['avg'] = alldata.mean(axis=1) #average different y values
plt.plot(alldata.index.values,alldata['avg'], color='black', linewidth=2) #plot averaged y values
against defined x axis
plt.xlabel('Binding Energy (eV)',fontsize=28) #figure criterea
plt.ylabel('Subtracted Counts (a.u.)',fontsize=28)
plt.xlim(293,282)
```

plt.ylim(0,2000)
plt.xticks(fontsize=24, rotation=0)
plt.yticks(fontsize=24, rotation=0)
plt.show()

	C-C position (eV)	C-C %Conc.	C-O position (eV)	C-O %Conc.	CO ₂ position (eV)	CO ₂ %Conc.	CO ₃ position (eV)	CO ₃ %Conc.
HPR 2- 1.75V	284.99 ± 0.04	19.5 ± 0.4	286.71 ± 0.05	15.8 ± 0.1	288.3 ± 0.3	2.2 ± 0.2	290.2 ± 0.2	5.9 ± 0.3
MPR 1.75- 0.6V	285.00 ± 0.06	16.3 ± 9	286.68 ± 0.07	16 ± 3	288.6 ± 0.7	2 ± 1	290.0 ± 0.1	7 ± 2
LPR 0.6- 0.02V	284.97 ± 0.04	22 ± 6	286.7 ± 0.1	10 ± 5	288.6 ± 0.5	3 ± 1	289.9 ± 0.4	5 ± 2
HPR FEC 2- 1.75V	285.00 ± 0.05	34 ± 3	286.7 ± 0.6	7 ± 1	288.5 ± 0.6	4.1 ± 0.9	N/A	N/A
MPR FEC 1.75- 0.6V	284.99 ± 0.02	26 ± 3	286.8 ± 0.1	10 ± 2	288.70 ± 0.07	5.9 ± 0.8	291.05 ± 0.09	2.4 ± 0.7
LPR FEC 0.6- 0.02V	284.96 ± 0.09	22 ± 3	286.9 ± 0.3	8 ± 2	288.7 ± 0.3	6 ± 2	290.7 ± 0.4	3.0 ± 0.7

Table S3.1. Quantification of carbon XPS data with peak position and peak concentration for a particular set of replicate experiments.

Note that HPR samples with FEC did not have a carbonate peak thus are marked N/A.

	O-C position (eV)	O-C %Conc.	O ₄ Cl position (eV)	O4Cl %Conc.
HPR 2-1.75V	531.6 ± 0.3	13.5 ± 0.2	533.3 ± 0.2	26.8 ± 0.1
MPR 1.75-0.6V	531.8 ± 0.2	15 ± 5	533.4 ± 0.1	26 ± 5
LPR 0.6-0.02V	531.5 ± 0.3	17 ± 7	533.3 ± 0.2	20 ± 10
HPR FEC 2-1.75V	531.1 ± 0.2	18 ± 4	533.3 ± 0.4	14 ± 4
MPR FEC 1.75- 0.6V	531.4 ± 0.4	9 ± 4	533.5 ± 0.3	24 ± 5
LPR FEC 0.6- 0.02V	531.4 ± 0.4	11 ± 6	533.4 ± 0.3	25 ± 9

Table S3.2. Complied quantification data from oxygen XPS results. The average peak position and peak area with their respective standard deviation are tabulated.

Table S3.3. Quantification data from the XPS spectra for sodium 1s electron listing the average peak position and peak area with their respective standard deviation

	Na position (eV)	Na %Conc.	NaF position (eV)	NaF %Conc.
HPR 2-1.75V	1072.1 ± 0.3	11 ± 4	N/A	N/A
MPR 1.75-0.6V	1072.2 ± 0.2	14 ± 5	N/A	N/A
LPR 0.6-0.02V	1071.8 ± 0.3	17 ± 4	N/A	N/A
HPR FEC 2-1.75V	1072.2 ± 0.2	6 ± 3	1073.9 ± 0.6	1.3 ± 0.7
MPR FEC 1.75-0.6V	1072.0 ± 0.1	10 ± 3	1073.3 ± 0.3	2.2 ± 0.8
LPR FEC 0.6-0.02V	1072.1 ± 0.3	13 ± 4	N/A	N/A

Note that NaF peak is not present when FEC is not present and LPR FEC signal was too convoluted to decipher a consistent NaF peak for accurate averaging and are thus marked with N/A.



Figure S3.5. Fluorine 1s XPS of 1 M NaClO₄ 1:1:1 EC: DMC: DEC +5% vol. FEC batteries cycled in HPR, MPR, and LPR. Each overlaid spectra have an average spectrum as a darker black line.
The fluorine peak at about $685.0 \pm 0.3 \text{ eV}$, $684.6 \pm 0.2 \text{ eV}$, $684.6 \pm 0.4 \text{ eV}$ for HPR, MPR, and LPR respectively, is NaF originating from FEC. The percent concentration for each of these peaks is $2 \pm 1\%$, $7 \pm 3\%$, and $5 \pm 1\%$, again for HPR, MPR, and LPR respectively. The HPR has a second fluorine peak at $687.5 \pm 0.3 \text{ eV}$ which is likely FEC that has not converted to NaF. It should be noted that there is no corresponding fluorinated carbon peak perhaps due to the lower RSF value of carbon compared to fluorine. When the high binding energy environment appears in the MPR and LPR attributed to carbonate appears there is no fluorinated carbon fluorine peak.



Figure S3.6. Chlorine 2p XPS of 1 M NaClO₄ 1:1:1 EC: DMC: DEC with (right) and without (left) +5% vol. FEC batteries cycled in HPR, MPR, and LPR. Each overlaid spectra have an average spectrum as a darker black line.

Chlorine 2p XPS peak was collected for all samples and no significant changes were observed as only the ClO₄ chlorine environment is observed.



Figure S3.7. Sodium 1s XPS spectra of as prepared for battery assembly, pristine sodium metal. Note there is no plasmon feature.



Figure S3.8. Top) In black, No FEC LPR sample HRES scan showing all of the sodium plasmon feature. In blue, pristine sodium metal as prepared for half-cell experiments. Bottom) Sodium

KLL auger peak from the same No FEC LPR sample shown in its entirety. Note that the binding energy of O1s (~532 eV) is present in this spectrum.

These large scan spectra are to show sodium auger (lower plot) and plasmon peaks (upper plot). The auger is important to recognize as the peaks in the oxygen spectra particularly the one at 537 eV and the one at 524 eV, which is too low in binding energy to be any type of metal oxide.



Figure S3.9. Carbon, oxygen, chlorine, fluorine, and sodium XPS spectra for antimony half-cell batteries with FEC cycled in the HPR (black), MPR (blue), LPR (red), and five full cycles (green).



Figure S3.10. Carbon, oxygen, chlorine, fluorine, and sodium XPS spectra for copper half-cell batteries with FEC cycled in the HPR (black), MPR (blue and red), and LPR (green).



Figure S3.11. Carbon, oxygen, chlorine, fluorine, and sodium XPS spectra for copper half-cell batteries with FEC cycled in for five cycles.



SI Figure S3.12. Carbon, oxygen, chlorine, fluorine, and sodium XPS spectra for copper halfcell batteries without FEC cycled in for five cycles.

Repeating cycling experiments and running XPS with different substrate is a different angle on understanding SEI formation. Included here in the dissertation is unpublished work with Cu and Sb substrates the compare with Cu₂Sb electrodes used throughout. Importantly, copper does not sodiate and functions as an unreactive electrode. This work is incomplete as certain conditions were never run but helps support hypotheses from the Chapter III and IV. Specifically, Figure S9 and S10 show the different potential regions with FEC using Sb and Cu as the substrate. The XPS results from these regions, with Sb and Cu, match what occurred with Cu₂Sb in Chapter III figures 3, 5, and 7. This means that FEC is likely functioning in a similar way as the same concentrations of SEI species are measured on the three different substrates. Furthermore, the fully cycled half-cells in figures S9, S11, and S12 also match the XPS data from other fully cycled batteries. These experiments begin to explore the role of substrate in SEI formation but more experiments with more diverse substrates are needed to fully understand how substrate affects SEI formation.

APPENDIX II: SUPPLIMENTARY INFORMATION FOR CHAPTER IV: SPONTANEOUS SOLID ELECTROLYTE INTERPHASE FORMATION IN UNCYCLED SODIUM HALF-CELL: USING X-RAY PHOTOELECTRON SPECTROSCOPY TO EXPLORE THE PRE-PASSIVATE OF SODIUM METAL BY FLUOROETHYLENE CARBONATE BEFORE APPLIED ELECTROCHEMSITRY

Experimental Detail

Cu₂Sb and Sb/CNT electrode preparation can be found in our previous publications.^{16,25,35} Battery assembly and sodium metal soaking experiments occurred inside an argon glove box (O₂ <1 ppm). Sodium metal (Aldrich, cubes mineral oil, 99.9%) is cleaned using a toothbrush to remove as much surface oxide as possible. The electrolyte solution comprised of 1 M sodium perchlorate (NaClO₄, Sigma Aldrich ACS Reagent) supporting electrolyte dissolved in 1:1:1 portions of ethylene carbonate (EC, recrystallized), dimethyl carbonate (DMC, Anhydrous Sigma Aldrich \geq 99%), and diethyl carbonate (DEC, Sigma Aldrich Anhydrous 99%) by weight, as well as for certain experiments, 5% fluoroethylene carbonate (FEC, Sigma Aldrich \geq 99%) by volume. The same FEC is used for presoaking sodium electrolytes. All sodium soaking is done in flame dried scintillation vials, no etching was observed in any experiment. Half-cell batteries are assembled using half inch Swagelok parts and cycled on Arbin BT2000 series battery tester under constant current conditions. Electrochemical impedance spectroscopy was performed using a Gamry Reference 3000 potentiostat between 300,000 and 0.1 Hz with 5 mV AC voltage.

Repeated from main text: Electrolyte condition **1** 1 M sodium perchlorate (NaClO₄) in 1:1:1 ethylene carbonate (EC): dimethyl carbonate (DMC): diethyl carbonate (DEC) a common electrolyte system. Condition 2 is 1 with 5% FEC. Finally, condition 3 has sodium metal is soaked in pure FEC for 48 hours before being used with condition 1.



Figure S4.1. Photograph electrolyte solutions immediately after sodium immersion. Electrolyte solutions are from left to right: 3, 2, and 1.

Images taken immediately after sodium is placed in all three electrolyte (1, 2, and 3) conditions show that the initial systems all look the same with pristine sodium that is still shiny from being brushed and clear electrolyte solutions (Figure S4.1).



Figure S4.2. Array of electrolyte component reactions using Teflon reaction wells. DMC, DEC, EC, FEC, VC, and PC, were mixed with No salt, NaClO₄. NaPF₆, or NaOTf and sodium metal. Left is an image within five minutes of immersion, the right image is ~72 hours later.

Sodium is soaked in different carbonates with and without different supporting electrolytes (Figure S4.2). The first row of DMC samples dried up, but the second row DEC shows a significant color change when a supporting salt is present. Third row EC is a solid, so no change occurs. Fourth row FEC has no color change with or without salt. Fifth row vinylene carbonate (VC) changes color both with and without salt. Finally, sixth row propylene carbonate (PC) only changed color with NaClO₄



Figure S4.3. H^1 NMR from solution of 1 M NaPF₆ in diethyl carbonate for ~5 months pictured right.

NMR of different electrolytes soaked with sodium were inconclusive (Figure S4.3, left). The NMR solvent used was CDCl₃ (Cambridge isotope laboratories, D 99.8%) where the supporting electrolyte salt crashed out, but organics are soluble. The example spectra shown is of DEC + 1M NaPF₆ (Figure S4.3, right), the most extreme example having shown an immediate color change in the Teflon array experiment as well as being left to sit for months to build up the products of the reaction. Unfortunately, the NMR spectra is dominated by the signal of DEC. A partially air free distillation was used to attempt to separate the products that caused the color change, but the solution had one fraction which condensed as a clear liquid. By NMR the distillation fraction was pure DEC. Leftover from the distillation was a colored solid which by XRD was NaPF₆. Additional careful air-free separations would need to be carried out to clearly identify any reaction products.



Figure S4.4. Left: carbon 1s XPS spectra of sodium metal soaked in different carbonates where EC-DMC mixture (black), FEC (blue), propylene carbonate (PC) (red), DMC (green) and DE (orange) are shown. Right: example picture of sodium metal soaked in DEC (left) and FEC (right).

XPS was performed on sodium metal soaked in various individual carbonates (Figure S4.4). In all cases, soaking sodium in carbonate without a salt resulted in solutions that remained clear. Many different carbon XPS environments including carbonate, carboxyl, singly oxygenated, aliphatic, and reduced carbon are observed with varying concentrations. This set of experiments shows the complexity of the sodium metal reaction with individual carbonates. These results clearly show the variability in reaction occurring between sodium metal and the different carbonates. Additional experiments are required to identify the products forming, to learn about their solubility, and understand how the presence of a supporting salt is capable of solubilizing these products to from initial SEI species.

Table S4.1. Quantification for all XPS data. Contains average peak position and % concentration as well as the corresponding standard deviation for all fit environments for no FEC (1) (orange), FEC (2) (blue), and Presoaked Na (green) systems (3). Contains both the Cu₂Sb (above) and the Na counter electrode (below).

Cu ₂ Sb NoFEC	Avg Position	Stdev Position	Avg Conc.	Stdev Conc.
C 1s C-C	284.99	0.04	15	3
C 1s C-O	286.66	0.06	13	2
C 1s CO ₂	288.3	0.2	2.4	0.6
C 1s CO ₃	290.1	0.1	5	1
Sb ₂ O ₃ 3d 5/2	530.10	0.09	0.3	0.3
Sb ₂ O ₃ 3d 3/2	539.44	0.09	0.2	0.2
Sb 3d 5/2	527.4	0.1	0.10	0.08
Sb 3d 3/2	536.8	0.1	0.06	0.05
O 1s ClO ₄	533.4	0.2	35	7
O 1s O-C	531.6	0.3	12	4
ClO ₄ 2p 3/2	208.5	0.1	3.0	1.0
ClO ₄ 2p 1/2	210.1	0.1	1.5	0.5
F 1s NaF	0		0	
F 1s FEC	0		0	
Na 1s	1072.4	0.2	12	2
Cu 2p 3/2	932.7	0.1	0.5	0.3
Cu 2p 1/2	952.7	0.2	0.21	0.10

Cu ₂ Sb FEC	Avg Position	Stdev Position	Avg Conc.	Stdev Conc.
C 1s C-C	285.02	0.05	28	6
C 1s C-O	286.7	0.1	7	2
C 1s CO ₂	288.6	0.1	7	1
C 1s CO ₃	290.4	0.4	3	2
Sb ₂ O ₃ 3d 5/2	530.5	0.1	2.5	0.6
Sb ₂ O ₃ 3d 3/2	539.9	0.1	1.6	0.3
Sb 3d 5/2	528.0	0.1	0.5	0.1
Sb 3d 3/2	537.3	0.1	0.35	0.06
O 1s ClO ₄	532.8	0.3	18	8
O 1s O-C	531.3	0.5	30	10
ClO ₄ 2p 3/2	208.4	0.2	0.9	0.2
ClO ₄ 2p 1/2	210.0	0.2	0.4	0.1
F 1s NaF	684.8	0.1	1.4	0.4
F 1s FEC	687.2	0.01	1.96	0.02
Na 1s	1072.0	0.1	7	1
Cu 2p 3/2	932.9	0.2	4	2
Cu 2p 1/2	952.7	0.2	2.1	0.8
Cu ₂ Sb Presoak	Avg Position	Stdev Position	Avg Conc.	Stdev Conc.
C 1s C-C	284.99	0.04	23	5

C 1s C-O	286.60	0.10	9	1
C 1s CO ₂	288.55	0.08	9	2
C 1s CO ₃	0		0	
Sb ₂ O ₃ 3d 5/2	530.6	0.1	2.0	0.8
Sb ₂ O ₃ 3d 3/2	539.91	0.10	1.3	0.5
Sb 3d 5/2	528.0	0.2	0.6	0.2
Sb 3d 3/2	537.3	0.2	0.4	0.1
O 1s ClO ₄	532.9	0.6	15	5
O 1s O-C	531.6	0.7	30	10
ClO ₄ 2p 3/2	208.8	0.7	2	1
ClO ₄ 2p 1/2	210.4	0.7	1.0	0.6
F 1s NaF	0		0	
F 1s FEC	687.4	0.1	2	1
Na 1s	1072.3	0.1	8	4
Cu 2p 3/2	933.2	0.1	2.3	0.9
Cu 2p 1/2	953.0	0.1	1.0	0.5
Na NoFEC	Avg Position	Stdev Position	Avg Conc.	
C 1s C-C	294.99	0.07	23	6
C 1s C-O	286.5	0.2	4.7	0.8
C 1s CO ₂	288.3	0.2	2.7	0.5

C 1s CO ₃	289.8	0.1	2.9	0.8
C 1s Cred	283.46	0.10	4	5
O 1s ClO ₄	533.4	0.3	7	5
O 1s O-C	531.6	0.2	16	7
O 1s Na ₂ O	530.0	0.3	13	4
F 1s NaF	0		0	
F 1s FEC	0		0	
ClO ₄ 2p 3/2	208.8	0.4	0.6	0.7
ClO ₄ 2p 1/2	210.4	0.4	0.3	0.3
ClO ₄ * 2p 3/2	207.2	0.3	1	1
ClO ₄ * 2p 1/2	208.8	0.3	0.7	0.5
Na 1s	1071.7	0.3	30	10
Na 1s Na ₂ O	1070.3	0.1	1.7	0.7
Na 1s NaF	0		0	
Na FEC	Avg Position	Stdev Position	Avg Conc.	Stdev Conc.
C 1s C-C	285.02	0.07	26	7
C 1s C-O	286.73	0.08	4	2
C 1s CO ₂	288.9	0.3	5	3
C 1s CO ₃	290.3	0.7	1.6	0.7
C 1s Cred	283.66	0.04	2.74	0.08

O 1s ClO ₄	533.13	0.26	25	8
O 1s O-C	531.1	0.3	12	5
O 1s Na ₂ O				
F 1s NaF	684.50	0.08	3.8	0.7
F 1s FEC				
ClO ₄ 2p 3/2	208.5	0.3	3	1
ClO ₄ 2p 1/2	210.1	0.3	1.5	0.6
ClO ₄ * 2p 3/2	0		0	
ClO ₄ * 2p 1/2	0		0	
Na 1s	1071.9	0.08	17	5
Na 1s NaF	0		0	
Na Presoak	Avg Position	Stdev Position	Avg Conc.	Stdev Conc.
C 1s C-C	285.01	0.07	18	5
C 1s C-O	286.8	0.3	3.3	0.9
C 1s CO ₂	288.6	0.2	2.3	0.7
C 1s CO ₃	289.8	0.4	2	1
C 1s Cred	283.7	0.2	3	1
O 1s ClO ₄	533.2	0.4	16	10
O 1s O-C	531.2	0.4	10	7
O 1s Na ₂ O	0		0	

F 1s NaF	684.6	0.1	10	5
F 1s FEC	687.2	0.4	7	4
ClO ₄ 2p 3/2	208.4	0.3	2.6	0.8
ClO ₄ 2p 1/2	210.0	0.3	1.2	0.5
ClO ₄ * 2p 3/2	0		0	
ClO ₄ * 2p 1/2	0		0	
Na 1s	1072.0	0.2	26	7
Na 1s NaF	1073.2	0.1	4.0	0.9

The error in peak position is low (<0.5 eV) meaning for replicate samples each peak fit is representing the same chemical environment. Peak position can then be correlated across different experiments to examine if the same chemical environments are in different samples. Percent concentration of each chemical environment has more error compared to peak position. This makes many comparisons the same within error across different samples, however, the important observations discussed in the main text are statistically significant.



Figure S4.5. Overlaid of XPS spectra of all spots on replicate uncycled Cu_2Sb from uncycled halfcells. Black line represents an average spectrum. The elements photoelectrons present are chlorine 2p (A, B, C), fluorine 1s (D, E, F) and copper 2p (G, H, I). The electrolyte systems in the uncycled batteries are the base electrolyte: 1M NaClO₄ 1:1:1 EC: DMC: DEC (A, D, G), base electrolyte with 5% FEC (B, E, H), and the base electrolyte with a the FEC pretreated sodium counter electrode (C, F, I).

The remaining XPS spectra for the other elements present in the uncycled Cu_2Sb half-cell sample are perchlorate chlorine, a small amount of sodium fluoride (condition 2 and 3 none for 1), and copper metal where the SEI is thin enough for it to be exposed (conditions 2 and 3 not 1) (Figure S5).



Figure S4.6. Overlaid of XPS spectra of all spots on replicate sodium metal from uncycled halfcells. Black line represents an average spectrum. The elements photoelectrons present are carbon 1s (A, B, C), oxygen 1s and antimony 3d (D, E, F) and sodium 1s (G, H, I). The electrolyte systems in the uncycled batteries are the base electrolyte: 1M NaClO₄ 1:1:1 EC: DMC: DEC (A, D, G), base electrolyte with 5% FEC (B, E, H), and the base electrolyte with a the FEC pretreated sodium counter electrode (C, F, I).

XPS spectra for carbon, oxygen, and sodium on the surface of the sodium counter electrodes from the uncycled half-cell experiments using electrolyte conditions **1**, **2**, and **3** (Figure S4.6). Unlike the surface of the Cu₂Sb the sodium metal surface does not have as many clear differences between the electrolyte conditions. The carbon spectra have five environments in all samples assigned as aliphatic, singly oxygenated, carboxyl, carbonate, and a reduced carbon environment. Peak positions are the same for the five carbon environments in the different conditions except for carboxyl, CO₂, carbon. Analogous with Cu₂Sb carbon XPS spectra, this environment is at 288.3 eV for **1** and at 288.6 for **2** and **3**. Further examining SI Table 1 where

quantification values are presented, the different electrolyte conditions have the same respective percent concentration of the five chemical environments within error. The presence of the reduced carbon environment is hypothesized to be a result of the highly reducing sodium metal surface. Oxygen contains a lot of heterogeneity but was for the majority of spectra fit with the same two environments: perchlorate, and carbon oxygen. Finally, there is a large sodium peak in all scans and a plasmon loss feature, showing the presence of metallic sodium, in certain spectra.



Figure S4.7. Overlaid of XPS spectra of all spots on replicate sodium metal from uncycled halfcells. Black line represents an average spectrum. The elements photoelectrons present are chlorine 2p (A, B, C) and fluorine 1s (D, E, F). The electrolyte systems in the uncycled batteries are the base electrolyte: 1M NaClO₄ 1:1:1 EC: DMC: DEC (A, D), base electrolyte with 5% FEC (B, E), and the base electrolyte with a the FEC pretreated sodium counter electrode (C, F).

XPS spectra for chlorine and fluorine on the surface of the sodium counter electrodes from the uncycled half-cell experiments (Figure S4.7). The chlorine spectra only contain perchlorate from the supporting salt. The fluorine is interesting as for condition **3** spectra there is a FEC fluorine environment in addition to the NaF in condition **2**. There is left over FEC from the presoak that was not removed when the sodium was dried. As this environment represented 7% very little FEC would not be able to change the bulk electrolyte and compromise the experiment.