Beyond Li: Challenges in moving towards earth-abundant battery materials

Thesis by Michelle Dena Qian

In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY Pasadena, California

> 2025 Defended May 16th, 2025

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Michelle Dena Qian ORCID: 0000-0002-4815-1014

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ACKNOWLEDGEMENTS

I have an extremely long list of people to thank. For my undergraduate research advisors and mentors–Prof. David Fox, Prof. Donna Whitney, Prof. William Seyfried, Prof. Christian Hartinger, Prof. Valerie Pierre, Dr. Andrew Haveles, Dr. Peter Scheuermann, Dr. Tasha Steel; thank you all for giving me the chance to work with and learn from you.

I would also like to give special thanks to Dr. Dima Huang who I worked with in my last few years of college–I started inorganic chemistry research in my junior year when the last time I'd taken a chemistry course was as a freshman. I am sure that I was extremely frustrating to work with, but I am so grateful that Dima stuck with me and I feel so lucky to have been able to befriend him. Dima, you are one of the most brilliant inorganic chemists I know in addition to being so intelligent, capable, and funny. Thank you for your candor, guidance, and support.

I must also thank Prof. Thomas Hoyes, my organic chemistry teacher and one of my undergraduate thesis committee members. Prof. Hoyes, your lab course was a huge turning point for me. The lessons I learned in persistence, analytical thinking, and learning from academic literature have served me well and will continue to aid me in my future pursuits. Your genuine love and curiosity for chemistry are incredibly apparent to your students and you were both an incredible instructor as well as research mentor, which can be a rare combination. Thank you.

Although I chose to study chemistry in graduate school, earth science has played a huge role in my life and truly, inorganic materials are just an extension of mineralogy. Prof. Kent Kirkby–thank you for being so open to chatting with a random high schooler about rocks and fossils, and for giving me the opportunity to teach the lab sections for your classes. I think back on those memories extremely fondly, and greatly admire your passion for teaching science in an engaging and narrative fashion. Thank you for sharing the joy of teaching with me,for your support, and for the best introductory earth science class I imagine any university has to offer.

Prof. David Kohlstedt–your rock and minerals physics class was my favorite course in college and continues to be relevant in my studies on inorganic materials. I am delighted to have known you and learned from you and while I am sorry that more students won't get to enjoy having you as a teacher, you have done more than enough and I hope you have the freedom to engage in any pursuit you would like (which I am sure continues to include rock and mineral physics). Thank you for helping me bridge the gap between earth science and materials chemistry, and for being such an invested, supportive instructor.

Prof. Josh Feinberg–as an instructor for my first geology field class as well as my mineralogy course, I have learned so much from you. You were also one of the first professors I really got to know as a person, and in addition to your wide breadth of knowledge on many earth science topics, your warm and encouraging personality made you a wonderful advisor. The impact your intro field geology course had on me is difficult to put into words. The class built my confidence as an independent researcher and in my ability to use my own skills and observations to unveil a scientific story. It also sparked my love for hiking and camping, which have been a great respite when graduate research has felt frustrating or begun to wear on me. Thank you for introducing me to the best and most welcoming sides of academia, as well as to the wonders of the outdoors.

In the line of earth science professors who have influenced me greatly, I want to give a big thank you to George Rossman–both for being my committee chair and rotation advisor, but for many other things in addition to those. Thank you for showing me how deeply intertwined inorganic chemistry and mineralogy are, and helping me realize the jump I thought I was making between earth science and chemistry was really just a switch in lenses for examining the same interesting concepts and problems. Thank you for your endless enthusiasm for your work and all the time you've spent talking with me in your office discussing ideas, and of course, interesting minerals. You are a joy to know and your curiosity and love for what you do are infectious.

Thank you to my advisor Kim for giving me this incredible opportunity. Your care for your students is extremely admirable, and you have cultivated a collaborative and welcoming group of amazing scientists. I have learned so much from you from including how to make a beautiful presentation and aesthetically-pleasing figures, how to think about scientific problems, how to organize and analyze next steps in experimental planning, and how to tell a scientific story. Thank you for everything you've done for me, for your understanding, and for believing in my abilities as a scientist.

Thank you also to the rest of my committee, Ryan Hadt and Karthish Manthiram, for your insightful questions and guidance throughout this process. I greatly value your input and encouragement, and feel lucky to have had such a kind and inspiring committee.

I have had the great privilege of working with many extremely talented scientists in the See group, and also being able to call them some of my closest friends. Broadly I would like to thank all See group members from all eras for creating a work environment that has been so fun and fulfilling to work in.

For our first graduates Josh and Steve, thank you for showing the way and continuing to be such helpful and supportive presences even in your post-Caltech careers.

Andy, our first post-doc-thank you for your mentorship and advice. You were a fantastic teacher and you will always be part of my first memory of working with the See group. I'm so glad you were the person there at 9 AM on my first day-thank you for letting me tag along with you to XRD, and for all your scientific guidance from then and until today.

Forrest, thank you for all of your help on my first project, as well as all the advice you've given me since then. You are so knowledgeable and even at my most stressed and panicked you have been a calming voice of reason. I can't imagine what my graduate school experience would have been like without you. I have loved getting to visit you, Aurora, Lupin, and Tonks in Oregon and see what sorts of things await me post-graduation.

Aurora-thank you as well for your advice and friendship. It has been so helpful to hear the experiences of another chemistry PhD and to see how you have navigated your career.

Wendy and Skyler, thank you for being such incredible role models. You are both such brilliant and capable women, in addition to being a lot of fun to be around. From DnD to High School Musical marathons and watching the solar eclipse, I have so many unforgettable memories with both of you.

Xiaotong-thank you for being so supportive and believing in me even when I felt unsure about myself; your students are lucky to have such a smart and caring advisor.

Christopher, you always have something insightful or unexpectedly hilarious to add to any conversation, and it has been such a privilege to witness your journey in this group. Thank you for also being a fantastic safety officer and reliable electrochemical expert.

Dan, you have been a phenomenal desk mate and I am grateful that I fought through to achieve your hard-won friendship. Minnesota and Canada are really not so different, though I concede that the Canadian pronunciation of 'portage' is correct.

Tori, it has been so lovely getting to know you both through DnD and especially on our last beamline trip together. I know you already know this, but you are truly such a thoughtful, intelligent, and caring person. Thank you for all your help and for being willing to talk me through things when I start to overthink!

I am so grateful for our newest post-docs, Abhiroop and Beichen. Both of you are so driven, smart, and funny, and I'm sad that I won't have more time in this group with both of you! However, it is so relieving to know that the lab is being left in such capable hands. Abhiroop, thank you for humoring me as I towed us back and forth across Pasadena to watch the Rose Bowl, and Beichen, thank you for joining in on craft night!

Similarly, I am thrilled to have our newest recruits join–George, Dawn, and Jason. The three of you are such a wonderful addition and I have no doubt that each of you will do great things in this group. Thank you for continuing to carry on the spirit of the See group I know and love.

I must also address the group that I have come to affectionately know as "the gang of youths." Colin, I am constantly in awe of the depth of knowledge you have for both your own project, as well as the level of detail you have in your suggestions and observations for the projects of others. You've really come into your own as a senior graduate student and I really believe in your ability to accomplish whatever you set your mind to. Thank you for sharing your joyful though somewhat impish grin with me, as well as for all your bird and plant facts. Please feel free to continue to send me geology questions!

Jadon, I've always been so impressed by your composure, insightful questions, and sharp wit, but your silliness is still one of my favorite things about you. I will always fondly remember our glovebox chats and will miss your unrepentant enthusiasm for the things that bring you joy. Thank you for introducing me to Pokémon TCG although I may eventually come to regret it.

Zion, your natural curiosity, love of learning and do-it-yourself attitude are so rejuvenating to be around, and are certainly the hallmarks of a great scientist. Thank you for allowing me to share my potentially factual trivia with you and for entertaining all my random tangents. You have also been a phenomenal new office addition!

I have to start a slightly different section to thank my lovely graduate mentees and

members (at some point) of the sodium subgroup. Nick, helping with your project has taught me so much and I hope I've managed to impart some wisdom and advice in turn. You are already so much more self-possessed, skilled, and knowledgeable than I was at the same graduate stage. You're also one of the funniest individuals I've come to know, and there's truly never a dull moment with you. Your creativity and ability to move forward in spite of less-than-ideal circumstances have been so inspirational for me; thank you.

Nai, you are so intelligent, organized, and confident. You're also incredibly funny, fiercely loyal, and constantly pushing yourself, and all of these characteristics make you a fantastic graduate student and loving friend. I know the beginning of graduate school has been difficult, but I also know your hard work, conviction in your desire to learn and research, and your perseverance will be rewarded. I will always be rooting for you and will always be here to tell you how capable you are if you need the reminder! I'm always smiling when I'm around you and I have loved talking on long drives, watching shows, and going to ceramics together. Thank you for showing me the wonders of the beach and the best parts of sunny California.

To both Nick and Nai, it has been an honor to work with the two of you and I am thrilled to know you two will become even better scientists than me.

I have also been lucky to work with and get to know some incredible undergraduate students during my tenure as a graduate student in the See group. Nayantara and Po-Jui, you are both such bright individuals who will be a great asset to wherever you go next. The levels at which you already plan, motivate, and understand your work are definitely already at graduate levels. Thank you for the opportunity to learn from and work with you!

Thank you to Abby, who I first met as an undergraduate in the See group. You have always been so cool and confident, and have really understood me in a way I didn't expect to find here. The community of queer Asian women can feel very small sometimes, but the love and care within it is so strong! It's been gratifying to know someone with so many shared tastes, and I can't wait to go to more concerts together and exchange more tattoo ideas. It's been so exciting to see you succeed and grow through your own graduate school experience, and I hope to visit you many more times in Boston while you're there. Likewise, you will always be welcome with me as a beloved house guest.

Thank you to Zac, whose support and unwavering faith have really gotten me through

some difficult times. From sharing mango sticky rice on my birthday to going to dinner in Alhambra when I was ready to give up on beam time, you have always managed to know when I really needed a friend. Having someone with me who can both remind me that things are not so serious but also that hard work is important when it's worth it has been invaluable for me especially throughout graduate school. Thank you for choosing me as a cat-sitter all those years ago, but moreover for your understanding, and I hope you know our friendship is unconditional both ways!

Thank you to Brian; you have always been willing to lend an empathetic ear. I could always rely on you to address my chemical safety paranoia, and whenever I hit a wall with experiments you were the perfect mix of cheerleader and pragmatist. As a fellow Minnesotan, talking with you also has the bonus of reminding me of home. Although getting two extremely introverted people to hang out together can be quite a task, I've always enjoyed any time I've spent with you. Quite honestly I think I have an incredibly strange sense of humor and I can think of no one better to share it with. You're an incredible scientist, friend, person, and I don't know if I know anyone else who cares as much as you do. I'm so grateful to have gotten to share an office with you all these years. Thank you for all the kindness and friendship you've given me.

Thank you to Kim Pham–you have really demonstrated what a life filled with hobbies and people you love can look like, and thank you for including me in that. It's been so inspiring to watch you spearhead an entirely new branch of science while also being number one cat mom and making some of the most beautiful art I've ever seen. You're such a gifted teacher who instructs with so much patience and care, and I feel really lucky to have been on the receiving end of that. Our office chats have always given me a much-needed boost in energy, and I can always count on you for a word of encouragement. Thank you for reminding me of the importance of creative outlets, for always being such a gracious hostess, and for being such a generous and supportive friend. Traveling together had left me with so many beautiful memories, and I look forward to many future trips together.

Thank you to Eshaan, who has showed me what it's like to have a brother. Your relentless positivity and the way in which you believe in me are things I hope to embody one day as well. Your enthusiasm for your work is infectious and I always love hearing you be so passionate about your projects and greater aspirations. Our late nights for beamtime preparation were always quite grueling, but spending them together with you managed to still made them a lot of fun. Science is hard but you've

always worked even harder, and I love that you try to lift other people up, too. I'll miss having you come bother me in lab or calling me to chat while you're in the glovebox. You have always prioritized the people and experiences in life that are really important; thank you for teaching me to do the same. Thank you for always seeing the best in me, and for being such an irreplaceable friend.

Thank you to Steven, who was my first friend in the See group and has seen me through everything. Thank you for taking a chance and agreeing to live with me in our first year, and for all our COVID walks through campus and climbing sessions at the tiny Caltech bouldering wall. Thank you for constantly entertaining my whims and letting me tag along with your own. I would have missed out on so many of the loveliest parts of Los Angeles and of life without you. You have such a talent for finding unique and exciting opportunities and rallying people for them, much to the benefit of everyone who knows you. Las Vegas and New Orleans came at times when I was in dire need of a break, and sharing those experiences with you made them even more rewarding. Thank you for always being on my side and by my side. I am so excited for you to finally get to rest a bit and enjoy the fruits of your labor!

Thank you to Jake, who has really been my day one. Thank you for all of your XPS assistance, for being the go-to car and fix-it guy, for our beach runs, but most of all for being an incredible friend. I always know I can rely on you and I love hearing your stories and making you laugh. Thank you for your book recommendations that always make me cry and provide me with an extra boost of optimism, and for always being willing to hear me out. Thank you for showing me the power of gratitude and the role it can play in shifting your whole mindset and perspective. It has gotten me through many trials and has improved my life so much. You're always looking out for other people, so I will always be there to look out for you!

Thank you to everyone in the Visiting Scientists program–Kitty, Mitch, all the scientists I've taught with–Jess, Aida, Cecilia, Chenyu, Channing, Andre, Honami, Luke, Pat–you are a guiding light for the future generations and the work you are doing is so important. Thank you for providing the space and opportunity for Caltech to contribute to the community and fostering a love of science in young students.

Andreas, my old roommate and most long-standing trivia companion–thank you for sharing your wit and whimsy. I have really loved getting to know you and look forward to keeping in touch and seeing where you land next.

Dan Mukasa, our friendship started fairly late but I can think of no one else I'd

rather have gone through an overnight layover in Miami with. Finding a kindred spirit here was so meaningful and I am truly grateful for our many introspective and reflective conversations.

Kay, it does feel like our eventual meeting and friendship was somewhat destined with our many mutual connections, and I feel so lucky that it finally happened! Thank you for your kindness, positivity, and your passion for your hobbies, science, and advocacy that motivate me to do more in kind.

Vince, thank you for the energy you bring to every gathering and conversation. You are so funny and outgoing, and I will always admire your ability to rapidly make friends in the most unlikely places. I cannot wait to be part of your wedding!

Chandler, I appreciate all of our book conversations, shared tastes and hobbies, and midwestern sensibilities. Thank you for putting up with how much I make fun of you while also being a deeply relatable and incredibly funny (yes, I said it) friend.

Ana, you are so kind and optimistic, and you inspire me to try new things and go to new places. Your enthusiasm always brings me such joy. Thank you for hanging out with me while I run errands, going shopping with me for conference outfits, and our many chats. I am so grateful to have met you and be able to call you a friend!

Rebecca and Cullen, some of the earliest friends I made in graduate school-thank you for your friendship as well as your insights as more senior graduate students. Thank you also for some truly memorable hiking and scuba diving experiences!

Sarah, thank you for inviting me to your iconic themed parties, sharing your renowned hosting and baking skills, as well as for our cat photo exchanges and lunches together.

Laura, thank you for our coffee catch-ups and being a fellow fast walker! You have a certain dignified nonchalance that I love and admire, and I am so happy that you've made your way back to the East coast that you love.

Anukta, you are so sweet and inspirational in how you strive to push your limits and explore new things. I'm not sure anyone else could have convinced me to do a half-marathon! I am also extremely grateful for your presence in both my life and Eshaan's, and am so excited to see what you will do next.

Clara, while I will forever be heartbroken that you didn't join the See group, I'm glad the Manthiram group has given you so many opportunities to shine. Thank you for being such a delight to mentor and for being an even greater delight to know and

confide in as a friend. I have faith in your ability to fast-track your PhD and move onto even more exciting things.

I have had the great joy of having many hobbies outside of research, and many lovely people to share them with. Matthew and Alice, thank you for introducing me to gardening at Caltech and for sharing your knowledge, home, and many cats with me.

Winston, I am so grateful to have met you while volunteering! Although we became friends quite late in my grad school career, you have been such a fun and caring presence and I have enjoyed all of our chats immensely.

To the members of the women's DnD group, many of whom are also past lab mates– Skyler, Wendy, Tori, and Marysol–thank you for introducing me to this new past time and providing a much needed space for embracing imagination, silliness, and gabbing.

Aline, you have been such a delightful addition to my craft nights and a beloved companion for watching shows, and I will miss our impromptu chats on the Beckman lawn.

Thank you to my many lovely friends from before graduate school for your continued love and support. Austin, I have so enjoyed our lengthy phone chats, your insightful takes, our occasional climbing sessions, and commiseration over the stresses of graduate school. You're almost there!

Anna, you have been such a constant in my life and I can always rely on you to make me laugh (frequently at myself), and I always feel that I have a home with you.

Radhika, our post-undergrad trip really kicked off my new start in graduate school, and you are so funny and empathetic, and I know you always have my back.

Jac, you have truly been with me from day one in graduate school, being by my side when I received my Caltech acceptance email. Being so much closer to you these past few years has been so much fun and I can never stop laughing when I'm with you. You always know how to make me feel better and/or knock some sense into me.

Bella, we've discussed it before but I remain extremely thankful for the fact that our paths re-intersected. Visiting you in NYC has been one of my continued highlights throughout graduate school.

Sruti, we have known each other for over fifteen years at this point and I am positive we will be friends for at least fifteen more–thank you for being the resident Minnesota expert, for always making me laugh, for your love, support, and friendship.

Ishi, having another friend outside of my own cohort going through a similar PhD program has been such an unexpected blessing, and I can always count on you to make my worries disappear and remind me of the things that really matter.

Thank you to my therapists, Sadaf and Dr. Ellen Miller-Kwon. I've learned so much about myself over these past six years, and have grown so much from our sessions.

Thank you to my parents and my older sister Caroline–you have all been tirelessly supportive of me and your love and care have always been reliable when I've felt my lowest. Thank you for fostering my love of learning from a young age and sharing your own experiences and advice with me from your own educational journeys.

Thank you all for everything. If I could go back and do it again, I wouldn't change a thing.

ABSTRACT

Batteries are a necessary component towards the advancement and proliferation of modern day technology, and are also an essential piece of the transition towards renewable energy. The lithium-ion battery (LIB) is the most common type of rechargeable battery, and the archetype relies on a traditional layered transition metal oxide cathode, organic electrolyte with a lithium salt, and a graphite anode. The design of these cells has been optimized to the point that the energy densities in these batteries are approaching their theoretical capacities. Combined with the supply chain challenges associated with many typical cathode elements and increasing energy demand, this highlights the need for new earth-abundant, high energy density battery technology. This thesis addresses challenges in two such systems: Mg-S and sodium-ion batteries (SIBs). Mg-S batteries suffer from capacity fade related to the polysulfide shuttle effect, which results in loss of active material and passivation of the anode. Here, we demonstrate that the rate of passivation is inversely proportional to the chain length of the polysulfides present in solution, and that passivation can be slowed or even reversed through addition of S_8 and the consequent perturbation of existing polysulfide speciation equilibria. SIBs are frequently touted as a "drop-in" technology for LIBs due to both systems relying on mobile alkali ions, but SIBs have inherently lower energy densities due to larger Na⁺ ion. In Chapters 3 and 4 we explore anion redox as a method of increasing energy densities in SIBs. Chapter 3 shows that in LiNaFeS₂, the charge compensation mechanisms from Li and Na cycling are identical. However, Na⁺ cycling is worsened compared to Li⁺ by structural degradation from the removal and insertion of the bulky Na⁺ ion, emphasizing the differences that exist between optimizing SIB cathode performance compared with that of LIBs. In Chapter 4, we aim to develop structure-property relationships that enable a stronger understanding of anion redox that can be leveraged to design high energy density, multielectron redox cathodes. Through the examination of the electrochemically inactive NaCu_{1.5}Fe_{0.5}S₂ and its vacancy-containing derivative NaCu_{1.125}Fe_{0.625}S₂, we show that vacancies in the transition metal layer enable redox although the redox is largely observed on the transition metals. The study also demonstrates potential limitations of ideal model systems and bulk spectroscopic analysis techniques in materials with low degrees of redox.

PUBLISHED CONTENT AND CONTRIBUTIONS

- Qian, M. D.; Laskowski, F. A. L. L.; Ware, S. D.; See, K. A. Effect of Polysulfide Speciation on Mg Anode Passivation in Mg-S Batteries. *ACS Appl. Mater. Interfaces* 2023, *15* (7), 9193. DOI: 10.1021/acsami.2c19488
 M.D.Q. participated in the conception of the project, collected and analyzed the data, and participated in the writing of the manuscript.
- Qian, M. D.; Patheria, E. S.; Dulock, N. V.; Morrell, C. T.; See, K. A. Alkaliindependent Alkali Anion Redox in LiNaFeS₂. *Chem. Mater.* 2024, *36* (16), 7953. DOI: 10.1021/acs.chemmater.4c01396
 M.D.Q participated in the collection and discussion of data and proofreading of the manuscript.

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INTRODUCTION

1.1 Motivation and Background

The global increase in electrification in conjunction with calls for divestment from fossil fuels has resulted in an increased demand for energy storage. Between 2002 and 2022, the percentage of the world population with access to electricity increased from 79.1% to 91.3%,¹ or the equivalent increase in population of nearly 2.3 billion people.² In order to meet the goals set by the 28th Conference of Parties of the United Nations Framework Convention (COP28) to combat greenhouse gas emissions and climate change, a large portion of the consumed electricity must be from renewable sources including wind, hydro, and solar.³ However, renewable energy does not come without drawbacks: one of the largest challenges is the offset between renewable energy production and demand, as many green energy sources are intermittent. The transportation sector also currently accounts for roughly 20% of greenhouse gas emissions,⁴ and decarbonization of transport is another important part of reaching the goals of the Paris Agreement and COP28.³

As such, batteries are both a ubiquitous part of modern life and a necessary component of the green energy transition. The current gold standard in rechargeable battery technology is the lithium-ion battery (LIB). First commercialized by Sony in 1991, the original LIB was comprised of a LiCoO₂ cathode, carbon-based anode, and electronically insulating organic electrolyte.⁵ LiCoO₂ is a layered material with alternating sheets of LiO₆ octahedra with sheets of CoO₆ octahedra. The general mechanism of a rechargeable battery is displayed in Figure 1.1, depicted with a graphite anode. Lithiated cathode materials are in a discharged state, and during charging, the cathode is oxidized and loses Li⁺ ions, which migrate through the electrolyte and across a physical separator where they are inserted in the reduced layers of the graphite anode. During discharge, this process is reversed.⁵ In order to charge compensate for the movement of the positive Li⁺ ions, electrons move through an external circuit. When a battery is discharged, a device connected to the external circuit may be powered.

Various improvements on LIB design have been made over the past few decades, notably including the introduction of LiFePO₄ (LFP) as a cathode. The capacity



Figure 1.1: Schematic of a typical LIB during charge. Li^+ ions are removed from the $LiCoO_2$ cathode and migrate (with anions, not shown for simplicity) towards the graphite. For charge compensation, electrons move from the cathode to the anode through an external circuit.

of LFP is significantly lower than that of its layered competitors (170 mAh g^{-1} compared with roughly 270 mAh g^{-1})⁶, but the low cost and toxicity of LiFePO₄ has given it increasing prominence in today's market.⁷

The difficulty with LIB technology largely stems from resource availability, energy independence, and sheer magnitude for energy storage demand. The majority of lithium produced is used in batteries.⁸ While the largest markets for LIBs are China, the United States, and the European Union,³ the global distribution of Li is concentrated in only three locations: China, Australia, and the so-called South American "Lithium Triangle" (Argentina, Bolivia, and Chile) which comprises 53% of the world's lithium resources.^{8,9} This predictably leads to significant volatility in the LIB supply chain,¹⁰ end even without the geographic politics, by some estimates supply-demand deficits for LIB materials including Li, Co, and Ni are expected to occur by 2030.¹¹ Although LFP does not rely on Co or Ni, it also suffers from a restricted supply chain due to 70% of phosphate rock reserves being located in Morocco and the Western Sahara; furthermore, the high purity phosphorus refinement necessary to produce LFP is primarily done in China, the United States, Kazakhstan, and Vietnam.³

The work of this thesis focuses on two kinds of earth-abundant, next-generation

battery systems: Mg-S and sodium-ion batteries (SIBs). Mg-S batteries couple a Mg metal anode with an elemental S cathode, typically in the presence of a liquid electrolyte (Figure 1.2). The high theoretical capacity of Mg-S batteries make them an extremely attractive candidate for future development; Mg anodes have theoretical gravimetric and volumetric capacities that are 5-6 times greater than those of graphite.^{5,12–14} The theoretical gravimetric capacity of the abundant, non-toxic S₈ cathode is likewise an order of magnitude greater than most LIB cathodes.^{15–17} Here, the major issue is the polysulfide shuttling effect whereby dissolved sulfur from the cathode speciates into polysulfides in solution, travels through the separator, and interacts with the metal anode.^{18–24} Further investigation into these processes is necessary to determine the best mitigation strategies.



Figure 1.2: Schematic of a Mg-S battery showing the relevant electrochemical reactions as well as the dissolution and migration of polysulfides across the separator to the anode and subsequent passivation.

In 2023, Hina launched the first SIB-powered electric vehicle (EV), and product launch and mass production announcements have come from CATL, BYD, and Northvolt. SIBs also have the potential to be 20-30% cheaper than LFP batteries.³

Work on SIBs generally focuses on framework cathode types such as Prussian blue analogues or layered transition metal oxides analogous to those used in LIBs.²⁵ HiNa and Faradion both use layered transition metal oxide cathodes, while Natron uses Prussian blue analogues.²⁵ Two major questions that require answers for successful promotion of SIBs are to what extent current LIB practices are applicable, and if there are methods to increase SIB energy densities to be competitive with LIBs.

1.2 Thesis outline

To this end, we turn towards emerging "next-generation" battery technologies that do not employ Li. Here we examine the Mg-S system and sodium-ion batteries (SIBs), two examples that rely on earth-abundant elements but face significant challenges in actualization and commercialization.

In Chapter 2, the interaction between Mg metal anodes and Mg polysulfides of varying lengths is examined. By tuning the Mg:S stoichiometry of Mg polysulfide precursors, differing distributions of polysulfide chain lengths are obtained. Mg plating and stripping in the presence of these polysulfides suffers from high overpotentials due to anode passivation, the rate of which is positively correlated with the proportion of short-chain polysulfides in solution. Addition of S₈ shifts the polysulfide equilibria to favor long-chain polysulfides and can even lead to the reversal of passivation. The nature of the Mg passivation is probed with HRSEM cross-sections, XPS, and electrochemical techniques.

In Chapter 3, differences between Li and Na-based anion redox are explored in the material LiNaFeS₂. Invoking anion redox is one method to increase cathode energy densities, but even in the more commonly studied Li systems the structure-property relationships underlying such charge compensation mechanism is unclear. By cycling LiNaFeS₂ against either a Li or Na half cell and enlisting a combination of electrochemical, diffraction, spectroscopic, and imaging techniques, we can determine to what degree knowledge on Li-based anion redox is transferrable and whether Na-based anion redox faces unique challenges.

In Chapter 4, the role of vacancies and notably, their structural location, in anion redox is investigated in the novel material NaCu_{1.5}Fe_{0.5}S₂. The constraints of the material structure restrict Cu vacancies to the transition metal layer, in contrast with previously studied materials in which the location of the vacancies could not be determined. Through the introduction of Cu vacancies, redox activity in the initially electrochemically inactive NaCu_{1.5}Fe_{0.5}S₂ can be unlocked.

Lastly, in Chapter 5, the conclusions of the previous chapter are summarized and their broader implications along with the general outlook for more earth-abundant batteries are discussed.

Chapter 2

EFFECT OF POLYSULFIDE SPECIATION ON MG ANODE PASSIVATION IN MG-S BATTERIES

Qian, M. D.; Laskowski, F. A. L.; Ware, S. D.; See, K. A. Effect of polysulfide speciation on Mg anode passivation in Mg-S batteries. ACS Appl. Mater. Interfaces 2023, 15 (7), 9193.

2.1 Abstract

Mg-S batteries are a promising next-generation system for beyond conventional Liion chemistry. The Mg-S architecture pairs a Mg metal anode with an inexpensive, high-capacity S₈ cathode. However, S₈-based cathodes exhibit the "polysulfide shuttle" effect, wherein soluble partially reduced S_x^{2-} species generated at the cathode diffuse to and react with the anode. While dissolved polysulfides may undergo reactions to form Li⁺ permeable layers in Li-S systems, the interfaces on Mg anodes are passivating. In this work, we probe the reactivity of various Mg polysulfide solutions at the Mg anode interface. Mg polysulfide solutions are prepared without any chelating agents to closely mimic conditions in a Mg-S cell. The polysulfides are synthesized by reacting Mg metal and S₈ in electrolyte and the speciation is controlled by varying the Mg:S precursor ratio. S-poor precursor ratios produce magnesium polysulfide solutions with a higher degree of short-chain polysulfides that react at the Mg anode faster than the longer chain analogues. Anode passivation can be slowed by shifting the polysulfide equilibria towards longer chain polysulfides through addition of S₈.

2.2 Introduction

Li-ion batteries currently dominate the market for both rechargeable portable devices and electric vehicles. ^{12,13,15,16} However, the capacity and cost of the Li-ion batteries is insufficient for long-range transportation and widespread grid-scale energy storage. ^{15,26,27} Magnesium metal anodes boast capacities higher than the commonly used graphite anode in Li-ion batteries with gravimetric capacities of 2205 mAh g^{-1} vs. 372 mAh g^{-1} for graphite and volumetric capacities of 3833 mAh cm⁻³ vs. 719 mAh cm⁻³ for graphite. ^{5,12–14} Li metal is another option for next-generation anodes, however, dendrite formation risks electrolyte ignition. ^{28–30} In contrast, Mg The Mg-S battery is a promising architecture that integrates a Mg metal anode with an Earth-abundant elemental sulfur, S_8 , cathode. S_8 is environmentally benign, widely abundant, ^{13,15–17,33,34} and has a theoretical gravimetric capacity of 1675 mAh g^{-1} assuming full reduction to the metal sulfide—almost an order of magnitude higher than contemporary Li-ion battery cathodes.^{15–17} Still, identifying an electrolyte simultaneously compatible with both electrodes remains a challenging problem in the Mg-S field. In the past few decades, several electrolytes enabling reversible Mg plating and stripping have been reported; however, Mg-S systems have additional complicating factors. Charge and discharge of the S₈ cathode involves the formation of soluble, partially reduced S_x^{2-} intermediates. S_x^{2-} anions, i.e. polysulfides, can migrate and diffuse to the anode and chemically react to become further reduced, decreasing the reversible capacity and viability of both Mg-S and Li-S batteries.^{18–24} Active material loss is also an issue in the analogous Li-S system, but lithium polysulfides in concert with other electrolyte additives can form beneficial solid-electrolyte interphases at the Li anode.^{35–37} In contrast, magnesium polysulfides (MgPS) passivate the Mg anode in Mg-S systems, thereby increasing stripping and plating overpotentials.^{38,39} The reaction of dissolved polysulfide species with Mg metal is suggested to form very stable surface layers containing MgS that passivate the surface.⁴⁰ The fast reactivity of dissolved polysulfide species at the Mg anode causes worsened self-discharge in Mg-S cells compared to Li-S cells.41

Understanding Mg anode passivation in Mg-S systems is non-trivial because polysulfides generally exhibit complex dissociation equilibria. Bieker *et al.* conducted the first study of chemically synthesized polysulfides in solvents relevant for Mg-S batteries.³⁹ They proposed the following generally accepted equations as governing Mg polysulfide speciation and equilibria:³⁹

$$4S_8^{2-} \rightleftharpoons 4S_6^- + S_8 \tag{2.1}$$

$$2S_8^{2-} \rightleftharpoons 2S_4^{2-} + S_8 \tag{2.2}$$

$$4S_6^{2-} \rightleftharpoons 4S_4^{2-} + S_8 \tag{2.3}$$

$$2S_6^{2-} \rightleftharpoons S_4^{2-} + S_8^{2-} \tag{2.4}$$

$$S_8^{2-} \rightleftharpoons 2S_4^{--} \tag{2.5}$$

$$\mathbf{S}_6^{2-} \rightleftharpoons 2\mathbf{S}_3^{--} \tag{2.6}$$

$$\mathbf{S}_4^{2-} \rightleftharpoons 2\mathbf{S}_2^{\cdot-} \tag{2.7}$$

The proposed reactions are in general agreement with the disproportionation reactions suggested by Tobishima *et al.* for alkali metal polysulfides.⁴² The equilibria are interdependent and temperature, concentration, and solvent dependent.^{21,39,42–45}

Interestingly, we have shown that the speciation of the polysulfide compounds has a significant effect on the rate of Mg passivation.³⁸ We recently demonstrated that elemental S_8 dissolved in electrolyte counter-intuitively causes lower deposition overpotentials at higher concentrations, suggesting that the reactivity is related to the polysulfide speciation.³⁸ We hypothesized that lower concentrations of S_8 are more likely to contain shorter chain polysulfides and thus the short chain polysulfides cause faster passivation of the Mg anode.³⁸ Higher concentrations of S_8 will favor the left side of equations 2.1-2.3, resulting in the promotion of long-chain polysulfide formation over short-chain polysulfides.

Here, we directly investigate the reactivity of various polysulfides chain lengths at the Mg electrode. MgPS solutions are prepared with varying distributions of polysulfide chain lengths without chelating agents and in conditions relevant to Mg-S cells. The reactivity of the MgPS solutions at the Mg anode is investigated by measuring deposition and stripping overpotentials at the Mg anode vs. a Ag_2S quasi-reference electrode. We show that solutions with short chain polysulfides cause higher overpotentials earlier in the cycling. Furthermore, we demonstrate that addition of S_8 reduces the overpotentials at the anode due to a shift in the speciation equilibria toward longer chain polysulfides.

2.3 Results and Discussion

Magnesium Polysulfide Synthesis

To investigate the reactivity of various MgPS molecules at the Mg anode, we must first prepare solutions of MgPS with varying chain lengths. Alkali polysulfides can be synthesized by reacting S₈ directly with reducing metals suspended in solvent.^{42,46,47} The reducing metal causes ring-opening reduction reactions to produce polysulfides.⁴² Although lithium polysulfides can be produced using either lithium metal or Li₂S as the reducing agent,^{21,28,39,42,48} Mg polysulfide synthesis is rare in literature. Mg polysulfides have been synthesized with a chelating agent *N*methylimidazole that helps solubilize Mg²⁺ in solution.^{28,39,49} However, solutions made with chelating agents may not accurately reflect polysulfide speciation in an electrochemical cell.

Therefore, we aim to prepare MgPS without the use of a chelating agent to more

accurately reflect the compounds that would be formed as intermediates in a Mg-S cell. A few examples of preparations without chelators can be found in the literature. Ford *et al.* synthesized polysulfides directly from Mg and S₈ powders in dimethoxyethane (DME) with 0.25 M MgTFSI₂ + 0.5 M MgCl₂ and suggested that the synthesis required the presence of magnesium salts. S₈ reduction to polysulfides was confirmed by UV-Vis.⁵⁰ Similarly, a MgS_x catholyte was prepared by reacting stoichiometric quantities of S₈ and MgS in tetraethylene glycol dimethyl ether with Mg(HMDS)₂, AlCl₃, and MgCl₂.⁵¹ One example of MgPS synthesis in neat solvent was reported by Zhao-Karger *et al.* in which Mg metal and S₈ powders were reacted in diglyme, however, no characterization of the polysulfides was shown.⁵²

The Mg salts in the solution likely activate the Mg metal surface and facilitate reactivity.⁵⁰ Thus, we explored the synthesis of MgPS directly in the magnesium aluminum chloride complex (MACC) electrolyte.⁵³ MACC is a good candidate electrolyte for the present study as it is prepared by a combination of the simple binary salts MgCl₂ and AlCl₃ and is non-nucleophilic.^{54,55} The MACC electrolyte has been shown to support reversible Mg plating and stripping at low overpotentials after electrochemical conditioning.^{53,56} The electrolyte in this study is composed of 30 mM AlCl₃ and 60 mM MgCl₂ in tetrahydrofuran (THF) and includes 10 mM of the chemical conditioning agent magnesium bis(hexamethyldisilazide) (Mg(HMDS)₂). The Mg(HMDS)₂ scavenges trace water and promotes formation of free chloride to activate the electrolyte.^{57,58} The electrolyte will be referred to simply as MACC–Mg(HMDS)₂ hereafter.

Mg polysulfides are synthesized by stirring Mg metal strips with S₈ powder in the MACC–Mg(HMDS)₂ electrolyte at 40°C under Ar for 7 days until a color change is observed. The ratio of Mg:S₈ is varied from a mole ratio of 1:2 Mg:S to 2:1 Mg:S to affect the resulting distribution of polysulfide chain lengths. The speciation is characterized with UV-Vis spectroscopy (*vide infra*). S₈-rich conditions (Mg:S 1:2) yield longer chain polysulfides and are thus called 1-MgPS solutions, and S₈-poor conditions (Mg:S 2:1) yield shorter chain polysulfides and are thus called s-MgPS. All polysulfide syntheses use S₈ in a 62.4 mM concentration of S. Previous direct synthesize Mg polysulfides with Mg powder in this system produce inconsistent results, and previous studies cite the passivation of Mg polysulfides in pure THF without the electrolyte salts, in electrochemically conditioned MACC, or from MgS

and S precursors were also unsuccessful. The free Cl^- generated by Mg(HMDS)₂ in combination with MACC has been hypothesized to activate Mg metal surfaces to promote facile Mg stripping and deposition, ^{57,58} and the same activation may be responsible for promoting the formation of Mg polysulfides.

Dissolved polysulfides are difficult to characterize as they can both disproportionate and oxidize.^{33,60} Many literature studies have relied on UV-Vis spectroscopy to characterize polysulfides.^{28,39,42,61,62} To characterize the MgPS solutions, the solutions are diluted with the MACC–Mg(HMDS)₂ electrolyte and analyzed using UV-Vis spectroscopy. The absorbance of the Cary 500 used for analyses saturates at roughly 125 mM S, and samples were diluted to accommodate this limit. Because dilutions will also affect the speciation, discussions of UV-Vis data are limited to qualitative and relative descriptions.

UV-Vis spectra for S₈, l-MgPS, and s-MgPS solutions in the MACC-Mg(HMDS)₂ electrolyte are shown in Figure 2.1 (an alternate representation of this data as difference curves with respect to S₈ can be found in Figure S1 in the Supporting Information). Several polysulfide species have more than one absorption peak and many of the absorption peaks overlap with other species. Disproportionation reactions preclude the isolation of any single polysulfide species for use as a standard.^{63,64} Despite the difficulty in assigning exact species, qualitative differences in speciation between the solutions can be observed in the UV-Vis spectra. Speciation of polysulfides is solvent dependent, ^{21,42,45} and so we focus on references in solvents with similar properties to THF (donor number = 20.0 kcal mol⁻¹, dielectric constant ϵ = 7.6).⁶⁵ THF absorbs below 250 nm,⁴² and only absorbances above 250 nm are used to identify species present in solution. Previous studies in a range of solvents including hexane, water, THF, dioxolane with DME, and tetraglyme attributed absorption in the range of 260-280 nm to elemental S_8 .^{39,42,61,62,66} In glymes, which have similar donor numbers and ϵ to THF, absorption close to 300 nm is assigned to S_6^{2-} , ³⁹ while absorption near 335 nm is assigned to either S_6^{2-} or the short-chain polysulfides S_2^{2-} , S_4^{2-} . ^{39,59,62,67} Here, absorbances observed in the 300 nm to 350 nm region are attributed to polysulfide species $S_{x<8}^{2-}$. The yellow color of many polysulfide solutions is the result of the S_4^{2-} chromophore, ⁴² and absorbs close to 400 nm in dimethylsulfoxide, glymes, and THF.^{21,62,66}

The UV-Vis spectra reveal the expected speciation trend. The S_8 solution displays prominent absorption corresponding to elemental S_8 . The l-MgPS solution shows similar features to the S_8 solution but with greater absorption in the region of long



Figure 2.1: UV-Vis spectra of S_8 , 1-MgPS, and s-MgPS solutions in the MACC-Mg(HMDS)₂ electrolyte. The data are shown with the electrolyte spectrum subtracted. The S_8 solution absorbs primarily 260-280 nm, while 1-MgPS and s-MgPS both show shoulders in the 335 nm region, with the shoulder in s-MgPS being much more prominent. Both 1-MgPS and s-MgPS also show some absorption at 400 nm, again with s-MgPS displaying a higher absorbance. Thus the 1-MgPS solution is composed of more long chain polysulfides compared to the s-MgPS, which has more short chain.

chain polysulfides, i.e. $S_{x<8}^{2-}$. The s-MgPS solution shows a greater proportion of short-chain polysulfides, with more prominent absorption features corresponding to $S_{x<8}^{2-}$ and S_4^{2-} . Electrochemical experiments are performed to determine the impact of these differences in speciation on Mg plating overpotentials.

Electrochemical Cycling of Polysulfide Solutions

In our previous work, we observed a counterintuitive result in that Mg anodes cycled in electrolytes with high concentrations of S_8 show lower overpotentials for Mg plating and stripping compared to low concentrations of S_8 .³⁸ We proposed that this was due to the speciation of S with higher S_8 concentrations favoring speciation to long-chain MgPS (equations 2.1-2.3) that reduce at the Mg anode

slower compared to short-chain MgPS. Thus, here we hypothesize that Mg metal stripping and deposition in l-MgPS will result in slower passivation than in s-MgPS. Chronopotentiometric experiments are used to examine the effect of polysulfide chain length on stripping and plating overpotentials.

We can now directly probe the relative reactivity of different distributions of polysulfides at the Mg anode using the synthesized polysulfide solutions. To evaluate the relative reactivity of the S_8 , 1-MgPS, and s-MgPS solutions at the Mg anode, we turn to an adaptation of the deposition and stripping protocol we developed previously.³⁸ Five cycles of alternating oxidative and reductive current are applied for 30 m intervals, followed by a 3 h open circuit voltage (OCV) rest period. We refer to a pair of oxidative and reductive currents as one cycle, with five cycles composing a set. A Ag_2S quasi-reference electrode is used to decouple anodic vs. cathodic overpotentials. Since the Ag_2S quasi-reference electrodes drift over time, the OCV rest period is used to probe the Mg/Mg²⁺ redox couple for calculating stripping and plating overpotentials. Polysulfide solutions at the same S concentration are cycled at a current density of ± 0.1 mA cm⁻², where S concentration is defined as the initial concentration of S used in the syntheses.

The ease of Mg plating is measured by the cathodic overpotential; however, the cathodic overpotential is convoluted by many competing reactions at the Mg anode when S is present in solution. Figure 2.2 summarizes the possible processes at the Mg | electrolyte interface. When the Mg working electrode is negatively polarized, the electrons can participate in a variety of reduction reactions (Figure 2.2) including the reduction of Mg^{2+} to Mg metal (plating),

$$Mg^{2+} + 2e^{-} \rightleftharpoons Mg_{(s)}$$
 (2.8)

reduction of dissolved elemental sulfur to long-chain polysulfides,

$$S_8 + 2e^- \rightleftharpoons S_8^{2-} \tag{2.9}$$

reduction of long-chain polysulfides to short-chain polysulfides,

$$aS_x^{2-} + 2(b-a)e^- \rightleftharpoons cS_y^{2-} + (c-b)S_{\frac{cy-ax}{c-b}}^{2-}$$
(2.10)

and reduction of polysulfides to MgS.

$$S_x^{2-} + Mg^{2+} + 2e^- \rightleftharpoons MgS + S_{x-1}^{2-}$$
 (2.11)



Figure 2.2: Schematic of the competing reactions at the $Mg|MACC-Mg(HMDS)_2$ + MgPS interface. Electrochemical processes at the interface may include the reduction of Mg^{2+} , MgPS, or the electrolyte. Mg may also react chemically with the polysulfides to form MgS. The reduction of short-chain polysulfides to MgS is proposed to proceed more quickly than reduction of long-chain polysulfides to MgS.

In addition to the electrochemical reactions, sulfurous species can also be chemically reduced by Mg metal to MgS.

While all of the possible reduction processes may consume electrons, the kinetically dominant reduction process will depend on and set the voltage of the working electrode in a galvanostatic experiment. When an electronically insulating layer is present on the working electrode, the resistance in the Mg|MACC-Mg(HMDS)₂ + MgPS|Mg circuit increases and necessitates higher overpotentials to support the same reactions.

First, we discuss the behavior of the neat electrolyte in the cycling experiment with no added S. The voltage curves during cycling for the control cell in neat $MACC-Mg(HMDS)_2$ electrolyte are shown in Figure 2.3(a). During the first set of cycles, anodic and cathodic potentials are near -1 and - 1.5 V vs. Ag₂S, respectively.



Figure 2.3: Potential transients measured during the standard cycling experiment of $Mg|MACC-Mg(HMDS)_2|Mg$ cells with a Ag_2S quasi-reference electrode. Electrolyte additives are varied with (a) neat electrolyte and electrolyte with added S_8 and (b) added l-MgPS and added s-MgPS. The results show that the rate of passivation is dependent on the polysulfide solution, with the solutions containing higher proportions of long-chain polysulfides passivating more slowly.

The OCV relaxation period is assumed to approximate the Mg/Mg²⁺ redox couple at -1.3 V vs. Ag₂S, and consequently the overpotentials for stripping and plating observed are less than 300 mV throughout the first set of cycling. Subsequent OCV periods stabilize at -1.4 V vs. Ag₂S, and the overpotentials decrease slightly from the initial set to less than 200 mV throughout the remaining 22 h. These results mirror those found for electrochemically conditioned MACC,³⁸ and confirm the previously reported high reversibility of the Mg/Mg²⁺ redox couple in the control MACC–Mg(HMDS)₂ system.⁵⁷.

Next, we discuss the effect of adding S_8 to the neat electrolyte. Figure 2.3(a) shows the potential transients with MACC-Mg(HMDS)₂ electrolyte with 62.4 mM S. The cathodic overpotentials eventually reach and stabilize at -2.6 V vs. Ag₂S due to the formation of a high impedance, passivating film on the surface of the Mg that is

likely MgS.³⁸ As soon as the cathodic transients plateau at -2.6 V vs. Ag_2S , the anodic overpotentials initially reach very high overpotentials upon polarization but decay over time. The oxidative behavior may be due to the oxidative stripping of the passivating layer that was formed on reduction.³⁸ These relatively stable anodic overpotentials for an Mg anode are in line with previous studies on Mg stripping and deposition in the presence of S_8 .^{38,68}

To determine if the speciation of polysulfides changes the passivation layer, the same cycling experiments are performed with 1-MgPS and s-MgPS present in the electrolytes. Figure 2.3(b) shows the potential transients measured in the MACC-Mg(HMDS)₂ electrolyte with l-MgPS and s-MgPS. The data measured in the electrolyte $+S_8$ is replotted for comparison. In the l-MgPS solution, the plating overpotential increases past the voltage measured in the S_8 solution to >-3 V vs. Ag_2S . The anodic potentials also jump to greater than 2 V vs. Ag_2S (2.5 V overpotential), and the OCV period transient begins to deviate from that of S_8 . The high plating and stripping potentials are observed until the end of the 56 h cycling period. The transients measured in the s-MgPS containing electrolyte show drastically different behavior. The Mg electrode reaches >-3.5 V vs. Ag₂S on the first cycle and the correlated anodic overpotentials are immediately observed. The processes causing polarization are therefore occurring much faster in the s-MgPS solution. The disparate behavior of the Mg electrode in the presence of the three different S-containing solutions suggests that polysulfide speciation is correlated with the rate of Mg anode passivation.

The Mg electrochemistry also depends on the polysulfide concentration. Figure 2.4 shows the potential transients measured with 1-MgPS and s-MgPS electrolytes at 62.4 mM and 39.9 mM concentrations of S. In both cases, the electrode reaches potentials of >-3 V vs. Ag₂S faster with higher polysulfide concentration, suggesting that the reactivity at the interface is dependent on the MgPS concentration. Due to the distinct evolution of the voltage transients that evolve with the 39.9 mM 1-MgPS, that electrolyte is selected for extensive characterization on the Mg anode surface. Physical characterization of electrodes cycled in the other solutions can be found in the Supporting Information.

Physical Characterization

To better understand the nature of the passivating layers formed during cycling, characterization methods including scanning electron microscopy (SEM), energy



Figure 2.4: Potential transients measured during the standard cycling experiment for $Mg|MACC-Mg(HMDS)_2 + MgPS|Mg$ cells with a Ag_2S reference electrode. Overpotentials are shown for cells with added (a) 1-MgPS and (b) s-MgPS. The low concentration solutions have S concentrations of 39.9 mM, and the high concentration solutions have S concentrations of 62.4 mM. The lower concentration polysulfide solutions reach electrolyte decomposition much slower than the higher concentration polysulfide solutions.

dispersive spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) are used. SEM, EDS, and XPS of electrodes cycled in neat $MACC-Mg(HMDS)_2$ can be found in the Supporting Information. The surface roughens slightly, and evidence of Cl and O are observed in the EDS. To characterize the surface after exposure to S-containing species, the surfaces of electrodes cycled in solutions with a bulk sulfur concentration of 39.9 mM S for the polysulfide solutions are characterized. For consistency, representative electrodes are characterized immediately following a 30 m cathodic step. Electrodes are rinsed with 1 mL of THF and dried in an Ar-filled glovebox for at least 2 days.

Electrodes from the l-MgPS solutions are selected for SEM analysis. The SEM image and corresponding EDS map of a Mg electrode cycled in l-MgPS until -2.65

V vs. Ag_2S are shown in Figure 2.5(a) and (b). The SEM reveals a pitted surface with depressions 20-40 μ m wide, some of which are filled with a mixture of Cl-, S-, and O-containing particles. No uniform layer is visible on the electrode surface, and the distribution of sulfur is highly variable. The Cl is attributed to electrolyte decomposition. The presence of O is the result of brief air exposure during sample transfer and could also be a product of electrolyte decomposition. To ascertain the presence of a passivating layer, cross-sections are milled using a gallium focused ion beam (FIB). Protective platinum is sputtered onto the sample surface prior to milling using an electron beam and ion beam. Figure 2.5(c) and (d) show cross-sections from a working electrode using high-resolution SEM (HRSEM). The surface is nonuniformly coated with the porous layer (see Figure S25). The cross-section shown in Figure 2.5(c) was taken from a lighter colored region of the sample when viewed by eye, while the cross-section in Figure 2.5(d) was taken from the grainy, darker layer. Figure 2.5(c) shows no interfacial layer between the Mg working electrode and protective platinum layers, but Figure 2.5(d) shows a layer of varying thickness from 0.16 to 0.38 μ m.

The Mg electrode can be cycled longer causing even higher overpotentials to be reached. The SEM image and corresponding EDS map for a Mg electrode cycled in 1-MgPS polysulfide solution until the cathodic overpotential reaches -4.20 V vs. Ag₂S is shown in Figure 2.6(a) and (b). The SEM image displays a highly irregular surface with almost no exposed bare Mg metal. S, Cl, and O distribution are more homogeneous than seen for the electrode cycled in 1-MgPS until -2.65 V vs. Ag₂S (Figure 2.5). A cross-section is milled to determine the thickness of this passivating layer. Figure 2.6(c) and (d) show the SEM images of the cross-sections from a working electrode cycled in 1-MgPS solution to -4.20 V vs. Ag₂S. The surface of this sample is much more irregular than for the electrode cycled to -2.65 V vs. Ag₂S, and cross-sections were taken from various regions on the electrode. An irregular layer between 0.11 and 0.29 μ m thick is observed in Figure 2.6(d), the layer is much thicker, roughly 3.84 μ m. Although the thickness varies, the layer is present across the entire electrode area.

XPS was performed to examine the chemical nature of the passivating layer. Both the Mg 2p and S 2p regions are examined, as shown in Figure 2.7. For electrodes isolated after cycling to -2.65 V vs. Ag_2S , three Mg environments are observed at 48.2, 49.3, and 50.5 eV. The 48.2 eV binding energy is assigned to a mixture of



Figure 2.5: Imaging and spectroscopy of Mg electrodes cycled in electrolyte with l-MgPS until the cathodic overpotential reached -2.65 V vs. Ag_2S . (a) SEM shows no surface film although the surface is pitted. (b) EDS maps for Mg, S, Cl, and O show that the Mg distribution is uniform with the exception of the non-conformal circular areas, which correspond to higher concentrations of S, Cl, and O. O is attributed to solvent decomposition and air exposure from transferring the sample into the SEM chamber. (c) HRSEM cross-section shows no passivating layer on the Mg surface. (d) HRSEM cross-section of a different part of the same electrode shows a new surface layer that is 0.16 to 0.38 μ m thick.

MACC–Mg(HMDS)₂ decomposition products and an Mn impurity in the overlapping Mn 3p region (see Figure S21), Mg, and MgO/MgS_x species, respectively.^{68–72} The S 2p region shows one $2p_{3/2}$ peak at 161.6 eV assigned to MgS_x species.^{52,73–75} For comparison, XPS of MgS was measured and can be found in Figure S31, and shows a more strongly reduced S 2p binding energy in alignment with previous assignments for alkaline earth sulfides.⁷⁶ Based on the layer thickness from HRSEM cross-sections, the more reduced MgS may be present beyond the detection depth of XPS. For an electrode cycled to -4.20 V vs. Ag₂S, two Mg environments are observed at 49.3 and 50.8 eV. The 49.3 eV peak is broad and assigned to mixed Mn


Figure 2.6: Imaging and spectroscopy of Mg electrodes cycled in electrolyte with 1-MgPS until the cathodic overpotential reached -4.20 V vs. Ag_2S . (a) SEM shows an insulating, highly non-conformal layer. (b) EDS maps for Mg, S, Cl, and O show less Mg than observed in the electrode cycled until -2.65 V vs. Ag_2S . S, Cl, and O are more evenly distributed across the surface than on the electrode cycled until -2.65 V vs. Ag_2S . The presence of oxygen is attributed to solvent decompoosition and brief air exposure. (c) HRSEM cross-section shows the layer thicknesses are between 0.11 to 0.29 μ m thick. (d) HRSEM cross-section of a different part of the same electrode shows a layer up to 3.84 μ m thick.

impurity and Mg, while the 50.8 eV peak is assigned to MgO/MgS_x. A S $2p_{3/2}$ peak is observed at 161.9 eV that is assigned to MgS_x.^{52,73–75}

The XPS results confirm that the passivating layer includes MgS_x species. In addition, based on the results of EDS analysis, the layer has a significant component of electrolyte decomposition products, corroborating the high overpotentials seen in electrochemical cycling. SEM, EDS, and XPS were also conducted on electrodes cycled in 62.4 mM S in MACC–Mg(HMDS)₂ and in s-MgPS and can be found in the Supporting Information. Similar results to 1-MgPS were observed for both solutions, although oxidized Mg- and S-containing species near 168 eV are observed



Figure 2.7: XPS of the Mg 2p and S 2p regions of Mg electrodes cycled until the cathodic overpotentials reached -2.65 V (a-b) and 4.20 V (c-d) vs. Ag_2S in l-MgPS solution. Both electrodes show evidence of MgS_x species.

on the electrode when S_8 is in solution in addition to MgS_x .

Effects of Sulfur Addition

So far, we have shown that Mg metal electrodes react with S-containing species to form high impedance surface films. When short chain polysulfides are present, the film is formed faster. Thus, shifting the equilibrium of S-containing species back to longer chain polysulfides should slow down passivation. To probe whether the polysulfide equilibria and subsequent passivation can be controlled, S_8 is added to the polysulfide solutions to shift the equilibria. Considering equations 2.1-2.3, we anticipate that addition of S_8 to the polysulfide solutions will push the equilibria to the left and favor long-chain polysulfide populations and thus lower cathodic

overpotentials.



Figure 2.8: Transient potentials measured from the 4 h before sulfur addition to 8 h after for symmetric Mg cells cycled in neat electrolyte and with 1-MgPS. All experimental cells are Mg|MACC-Mg(HMDS)₂ (+ polysulfides)|Mg with a Ag₂S quasi-reference electrode. The x-axis $(t-t_{S_8})$ represents the hours of cycling elapsed in relation to the time of sulfur addition. (a) S₈ addition to neat electrolyte results in plating overpotential increases, while S₈ addition to 1-MgPS results in overpotential suppression. (b) Both cells contain added 1-MgPS, with one undergoing sulfur addition and the other left as a control. At 0 h, both cells have reached plating overpotentials of roughly 1.9 V. With no added S₈, at $t-t_{S_8}>0$ h plating overpotentials are suppressed to 550 mV. These results show that plating overpotentials can be controlled via S₈ addition. Full cycling data can be found in the SI.

To measure how S_8 addition affects the Mg electrodes, S_8 is added at a concentration of 312 mM S during cycling after the passivating layer has developed as indicated by cathodic potentials reaching >-2.6 V vs. Ag₂S (Figure 2.8). S₈ addition to neat electrolyte MACC-Mg(HMDS)₂ (black) and electrolyte with added 1-MgPS (red) are shown in Figure 2.8(a). After S₈ is added, the cathodic overpotentials in MACC-Mg(HMDS)₂ increase from 200 mV to 500 mV, while the cathodic overpotentials in the electrolyte with added l-MgPS decrease drastically from 1.9 V to 550 mV. Figure 2.8(b) shows cycling data for l-MgPS with and without added S_8 . At 0 h, both cells have reached cathodic overpotentials of roughly 1.9 V. Slight differences in electrochemical behavior are due to variation in electrode area. With no added S_8 , at *t*-*t*_{S8}>0 h cathodic overpotentials remain near 1.9 V, and anodic overpotentials begin to increase. In the cell with added S_8 , at *t*-*t*_{S8}>0 h cathodic overpotentials remain near 1.9 V, and anodic overpotentials are suppressed to 550 mV and oxidative overpotentials remain constant. These results show that S_8 addition can effectively be used to control polysulfide speciation equilibria and reverse passivation. Based on equations 2.1-2.3, S_8 addition promotes the formation of long-chain polysulfides. Therefore, these findings also support the conclusion that long-chain polysulfides passivate slower than short-chain polysulfides.

2.4 Conclusions

We show that Mg passivation rates are dependent on polysulfide speciation. Polysulfide speciation can be altered in synthesized solutions by varying the input Mg:S ratio, with lower proportions of S correlating to larger proportions of short-chain polysulfides. Short-chain polysulfides are likely preferred because their charge density can be more efficiently compensated by divalent Mg²⁺ in a low dieletric, low-donor solvent like THF. Furthermore, the results show that the initial proportion of polysulfide species impacts subsequent cycling behavior. Rate of overpotential increase is inversely correlated with chain-length of polysulfides in solution – s-MgPS contains the largest population of short-chain polysulfides and experiences rapid overpotential growth. This supports our previous hypothesis that MgS passivation product formation is easier by reaction with short-chain polysulfides than long-chain polysulfides.^{38,41} Reduction of short-chain polysulfides to MgS is a less intensive reaction with respect to the number of electrons transferred leading to faster reduction kinetics compared to reduction of longer-chain polysulfides. Through SEM imaging and XPS, the thin passivating layer at overpotentials of 1.6 V is determined to be irregularly deposited MgS_x , MgS, and chlorine-containing electrolyte decomposition species. The thicker passivating layer at overpotentials greater than 2.5 V contains both MgS_x and large quantities of electrolyte decomposition products.

Addition of S_8 shifts polysulfide speciation equilibria towards long-chain polysulfides, and thereby suppresses cathodic overpotential growth. Addition of S_8 reduces overpotentials by >1 V when added to an electrolyte with dissolved l-MgPS. Although Mg metal passivation in Mg-S batteries is a recognized problem,^{40,41,50} the

present study suggests that the passivation rate will be dependent on the S speciation. Overall, these conclusions provide insight into the complexity of polysulfide equilibria and reactions during cycling. The mechanisms for interfacial passivation may inform other next-generation battery designs reliant on charge-dense cations.

2.5 Experimental Polysulfide Synthesis

The MACC electrolyte was prepared in an Ar-filled glovebox according to Barile *et al.* with the addition of Mg(HMDS)₂ as in Kim *et al.* in 20 mL batches.^{56,57} Tetrahydrofuran (THF, 99.9%, Fisher Scientific) was dried in a Pure Process Technology solvent purification system, and anhydrous AlCl₃ (99.999%), MgCl₂ (99.9%), and Mg(HMDS)₂ (97%) were purchased from Sigma-Aldrich and Fischer Scientific, respectively. Solutions of MACC–Mg(HMDS)₂ (30 mM AlCl₃ + 60 mM MgCl₂ + 10 mM Mg(HMDS)₂) were prepared by adding 10 mL of chilled THF (cooled to approximately 0°C on a Peltier plate) dropwise to anhydrous AlCl₃ (80 mg). THF (10 mL) was added to anyhdrous MgCl₂ (114.3 mg) and allowed to stir for 1 minute. The AlCl₃ was completely dissolved in THF to yield a colorless solution. The AlCl₃ and MgCl₂ solutions were combined and the resulting solution was stirred at 420 rpm until clear and colorless (≥6 hours). The electrolyte was subsequently conditioned by adding Mg(HMDS)₂ (69 mg) and allowed to stir until clear.

To synthesize Mg polysulfides, the oxide layer of Mg metal was scraped off using an X-acto blade, and then cut into small ($<1 \text{ cm}^2$) pieces in an Ar-filled glovebox. The Mg pieces (22.8 mg and 91.0 mg for Mg:S 1:2 and 2:1, respectively) were combined with sulfur powder (60 mg) in a Schlenk tube, and 30 mL of MACC–Mg(HMDS)₂ was added. The solution was subsequently heated to 40°C and stirred under Ar for 7 days until a color change from clear to yellow was observed. The Mg polysulfides were then brought back into the glovebox and centrifuged three times in five minute cycles, with the Mg polysulfides being carefully decanted into new tubes between each cycle. All polysulfide syntheses used a 62.4 mM concentration of S.

1-MgPS polysulfide experiments utilized two batches of 1-MgPS (UV-Vis shown in SI). The second batch was more dilute than the first, and the solution was concentrated by slow evaporation to achieve a concentration close to the first batch.

UV-Vis Measurements

Solutions were diluted to a nominal concentration of 6.24 mM S for UV-Vis measurements unless otherwise noted. UV-vis measurements were measured on a Cary 500 spectrometer in screw cap cuvettes with a 1 cm path length. The $MACC-Mg(HMDS)_2$ in THF electrolyte spectrum was subtracted as the background.

Ag₂S Quasi-Reference Electrode Preparation

Ag₂S quasi-reference electrodes were prepared according to literature precedent.^{38,77,78} Aqueous $(NH_4)_2S$ (5 wt %) was diluted from a 40-48 wt % stock (Sigma-Aldrich) with deionized (DI) water. The solution was sparged for 30 minutes with Ar. Ag wires (99.9%, Sigma-Aldrich) were cleaned with 1500 grit silicon carbide paper (McMaster-Carr) and subjected to a single reducing chronoamperometry step at -0.5 V vs. a Ag/AgCl reference electrode in 1 M aqueous KCl solution for 2 minutes to remove surface oxides. The Ag wires were then rinsed with DI water prior to submersion in the $(NH_4)_2S$ solution for 24 hours while sparging with Ar.

Electrochemical Testing

All electrochemical cells were prepared in an Ar-filled glovebox. Electrochemical experiments were conducted on a VMP3 potentiostat (Bio-Logic). Three-electrode cells with an Ag_2S quasi-RE and Mg foil (99.9%, MTI) working electrode (WE) and counter electrode (CE) were assembled in 1.8 mL screw-thread borosilicate vials (VWR) with 1.5 mL of electrolyte. WE surface area was measured by taking a photograph of the cell and measuring the submerged area using ImageJ. Cells were cycled at a current density of 0.1 mA cm⁻². WE surface area varied between experiments but generally was maintained between 0.4 – 0.6 cm².

Electrochemical Testing with S₈ Addition

All electrochemical cells were prepared in an Ar-filled glovebox. Electrochemical experiments were conducted on a VMP3 potentiostat (Bio-Logic). For initial sulfur addition, S was added at a concentration of 312 mM to 1.5 mL of Mg polysulfides (or 1.5 mL of MACC–Mg(HMDS)₂ with S₈ for the elemental sulfur studies), and cycling proceeded as previously described. For S addition after MgS passivation, three-electrode cells as previously described were cycled until overpotentials reached 1.6 V, at which point the experiment was paused, 10 mg mL⁻¹ of S₈ was added, and the cells were reassembled with the same WE, CE, and quasi-RE. For longer experiments, some solvent evaporation was observed over time. THF was added as needed to maintain a total volume of 1.5 mL and minimal voltage shift (<60 mV) was observed during THF addition. After solvent addition, the cell was then allowed to rest at OCV for 3 hours prior to continuation of the experiment. All S addition

experiments were run in at least triplicate.

SEM and EDS

All characterization was completed on working electrodes after rinsing with 1 mL of THF and drying in an Ar glovebox for at least two days. Samples were briefly exposed to air during transfer into the instrument. SEM images were taken with a ZEISS 1150 VP field emission scanning electron microscope with a 15 kV accelerating voltage and an in-lens secondary electron detector. EDS data were collected using an Oxford X-Max SDD X-ray energy dispersive spectrometer with a 15 kV accelerating voltage.

HRSEM Cross-sections

All characterization was completed on working electrodes after rinsing with 1 mL of THF and drying in an Ar glovebox for at least two days. Samples were briefly exposed to air during transfer into the instrument sample holders. Images were taken with a Nova 600 NanoLab equipped with a field emission gun (FEG), scanning electron microscope (SEM), and gallium focused ion beam (Ga-FIB). Prior to milling cross-sections, all samples were protected with a layer of electron beam deposited platinum and ion beam deposited platinum using a gas injection system (GIS).

MgS Synthesis

All materials and precursors were handled inside an Ar-filled glovebox. MgS was prepared by solid-state synthesis similar to Kobayashi *et al.*⁷⁹ Mg (Alfa Aesar, 99.8%) and S (S₈, Acros Organics, >99.5%) powders were ground in stoichiometric quantities and pressed into a pellet of 300 mg with a hand-operated arbor press. The pellet was placed inside a vitreous silica ampule, evacuated to ≤ 10 mTorr, and sealed with a methane-oxygen torch without exposure to air. The ampule was heated at 2°C min⁻¹ to 600°C with a dwell time of 24 h. After ambient cooling to room temperature, the ampule was opened inside the glovebox, ground into a fine gray powder, and determined to be phase-pure by X-ray diffraction (XRD). Samples for characterization were mounted on glass slides with polyimide tape to prevent air exposure, and XRD was performed using a Panalytical X'Pert Pro with Cu K α radiation.

XPS

Each XPS sample was rinsed with 1 mL of THF (Sigma Aldrich, 99.5%) and dried

under ambient glovebox conditions for at least 48 hours before analysis. XPS data for 1-MgPS were collected using a Surface Science Instruments M-Probe ESCA controlled by Hawk Data Collection software. Low-resolution survey spectra were acquired between binding energies of 1-1000 eV. Higher-resolution detailed scans, with a resolution of 0.08 eV, were collected on individual XPS lines of interest. The sample chamber was maintained at $<2 \times 10^{-8}$ Torr. The XPS data were analyzed using CasaXPS analysis software, and individual peaks of interest were fit with Shirley backgrounds. Peaks were fit using asymmetric Gaussian-Lorentzian line shapes. Adventitious carbon was calibrated to 285 eV. S 2p peaks were fit as doublets with a 1.2 eV splitting.⁷⁵. Mg 2p splitting is on the order of 0.28 eV.^{80,81} No effect in assignment was seen without taking spin-orbit splitting into account and Mg 2p peaks were fit as singlets.

X-ray Fluorescence

A Mg foil was manually abladed to remove surface oxides. XRF analysis of the foil was performed with a Micro-XRF Spectrometer (Bruker M4 TORNADO).

2.6 Acknowledgements

M.D.Q. acknowledges support from the National Science Foundation Graduate Research Fellowship under Grant No. DGE1745301. F.A.L.L. acknowledges the support of the Arnold and Mabel Beckman Foundation via a 2020 Arnold O. Beckman Postdoctoral Fellowship in Chemical Sciences. K.A.S. acknowledges support from the David and Lucile Packard Foundation.

Chapter 3

ALKALI-INDEPENDENT ANION REDOX IN LINAFES,

Qian, M. D.; Patheria, E. S.; Dulock, N. V.; Morrell, C. T.; See, K. A. Alkaliindependent Alkali Anion Redox in LiNaFeS₂. *Chem. Mater.* 2024, 36 (16), 7953.

3.1 Abstract

Although Na-ion batteries present a promising and more sustainable solution compared to Li-ion batteries, Na-ion batteries have comparatively lower energy density and suffer from irreversible charge storage due to the size and mass of Na⁺. In recent years, the investigation of Li-rich materials has revealed employing multielectron redox that couples cation and anion redox is a method to improve capacity. Coupling anion and cation redox could be a way to improve the low energy density of Na-ion cathodes, but the influence of the large Na⁺ on these electrochemical processes is not well understood. Here, we leverage the mixed-alkali nature of LiNaFeS₂ to compare its behavior in Li vs. Na half cells. LiNaFeS₂ is known to support multielectron redox by virtue of cation and anion redox in Li half cells. We now demonstrate that LiNaFeS₂ can also be used as a multielectron Na cathode. Elemental analysis of the cathodes at various states of charge verify Na as the dominant mobile ion after first charge, which correlates to deviations in the electrochemistry compared to the material cycled in a Li half cell. Notably, cycling with a Na electrolyte causes the particles to roughen and amorphize. Fe and S K-edge X-ray absorption spectroscopy show that the charge compensation mechanisms from an electronic structure point of view are fundamentally the same independent of cell configuration. Significant structural differences between the Li and Na half cells are observed and further probed with synchrotron X-ray diffraction studies, scanning electron microscopy, and cyclic voltammetry coupled with b-value analysis. Our work provides a fundamental study on the differences between Li- and Na-based anion redox in the same material.

3.2 Introduction

In response to the climate crisis, a global effort to replace fossil fuels with more renewable energy sources has risen over the past few decades. Electrification based on renewable sources like wind, solar, and hydro necessitate grid-scale energy storage based on low-cost and sustainable materials.^{82–84} Although Li-ion batteries (LIBs) dominate the market for vehicles and personal electronics, the cost and availability of LIB materials poses a significant obstacle towards applications in large-scale stationary energy storage.^{85,86} The crustal abundance of Li is only 20 ppm, and in practice the accessible Li reserves are geographically restricted with 53% of identified Li reserves residing in Argentina, Bolivia, and Chile.^{87–90} The market for Li is also especially volatile, with prices of battery-grade Li₂CO₃ fluctuating between \$8,600 and \$68,100 per metric ton (a 692% variation) within the past five years.^{86,88} In contrast, Na has a crustal abundance of 23,600 ppm and is distributed globally.⁹¹ Compared to Li, Na₂CO₃ prices ranged from \$120.99 to \$161.95 per metric ton (a 34% variation) from 2019 to 2023.⁸⁸ Na-ion batteries (SIBs) thus provide an opportunity to significantly decrease battery materials costs and enable energy storage independence.

Despite its many advantages, the main drawback in SIBs compared to LIBs is a significant drop in theoretical energy density. The Na analogs of Li materials have lower gravimetric and volumetric energy densities as a result of Na possessing both a larger molar mass and ionic radius than Li (23 g mol⁻¹ and 1.02 Å vs. 7 g mol⁻¹ and 0.76 Å, respectively), in addition to a less negative standard reduction potential (-2.7 V and -3.0 V vs. SHE, respectively).^{87,92,93} One strategy to compensate for this is the employment of multielectron redox that leverages both cation and anion redox in one material. Anion redox has received considerable attention in LIB research on layered transition metal oxides and more recently in sulfides. Anion redox depends on the positioning of hybridized metal d and ligand p bands. In the oxides, it is believed that depending on the degree of overlap, oxidation of the ligand band may be stabilized.^{94–96} However, the presence of non-bonding p states is also thought to increase the likelihood of stable anion oxidation, and has been promoted through the introduction of vacancies⁹⁷ or more ionic metal-ligand interactions via metal substitution.^{94,98,99} Vacancies have been shown to be directly correlated to anion redox in sulfides, which results in the formation of a persulfide bond.⁹⁷ Further, we have shown that despite substitution of Fe for Co in alkali rich sulfides, the anion oxidation voltage does not shift which is strong evidence that anion oxidation occurs from non-bonding bands.¹⁰⁰

Anion redox has also been studied in Na transition metal chalcogenide materials, but to a significantly lesser extent and often only in the single electron redox context.

Na-rich layered oxides such as Na₂RuO₃,¹⁰¹⁻¹⁰³ Na₃RuO₄,¹⁰⁴ and Na₂IrO₃ have been reported to undergo multielectron redox with anionic contributions, but the abundance and cost of the 4d and 5d transition metals employed make them impractical for applications outside of academic interest⁹⁰ and in Na₂IrO₃, the degree and nature of the anionic redox is unclear.^{105,106} Na₂Mn₃O₇ is a promising anion redox material that exhibits relatively small hysteresis in the anion redox region, but the mechanism appears to rely heavily on the specific ordering present in the structure and may be challenging to replicate as a design principle for new materials.^{107–114} Anion redox has been invoked as the working mechanism in several NaMnO₂ substituted materials,^{115–117} but NaMnO₂ still shows low capacity due to the 1:1 stoichiometric ratio of Na:Mn. Although anion redox is primarily reported in oxides, the high voltages required confounds the ability to probe the mechanism with deleterious side reactions and electrolyte decomposition.^{118–124} As such, our group has focused on studying multielectron anion redox in Li transition metal sulfides stemming from the original Li-rich metal sulfide material $Li_2FeS_2^{125-133}$ including the Li₂FeS_{2-y}Se_y ($0 \le y \le 2$) solid solution ^{125,134} and LiNaFeS₂. ^{125,135}

Work in anion redox in Na transition metal sulfides is also limited. Shadike et al. reported layered NaCrS₂ as a Na cathode that undergoes purely anionic redox to reversibly extract approximately 0.5 equivalents of Na⁺. They proposed that Cr migration to vacated Na positions during charge creates a Cr/V'_{Na} antisite and Na-S-□ configuration that liberates non-bonding S 2p bands and promotes anion redox.¹³⁶ The authors published additional work on the NaCrS_xSe_{2-x} (x = 0.5, 1.0,and 1.5) solid solution and on NaCrS₂ substituted with Ti or V to probe the effect of metal-ligand overlap on the consequent charge compensation processes. 95,137,138 Nasu et al. reported multielectron anion redox in the material Na₂FeS₂ with a solid state electrolyte, Na₃PS₄, but the mechanism has not been shown in a conventional liquid electrolyte cell.¹³⁹ Leube *et al.* synthesized both Na_2TiS_3 and Na_2ZrS_3 and found that the former can undergo anion redox whereas the latter is electrochemically inactive.¹⁴⁰ Interestingly, Li₂TiS₃ is electrochemically inactive^{141,142} and while the authors propose that increased S lattice distortion from the larger Na makes anion redox accessible, they do not establish a mechanism through which the anion redox occurs.¹⁴⁰ Thus, anion redox in Na transition metal sulfides remains relatively unexplored.

Here, we revisit $LiNaFeS_2$ as a cathode in both Li and Na half cells to probe differences in anion redox based on the mobile alkali ion. $LiNaFeS_2$ crystallizes in

the $P\bar{3}m1$ space group and is composed of tetrahedral metal/Li layers alternating with octahedrally coordinated Na layers. Li and Fe share the tetrahedral sites with 50/50 occupancy while all Na occupies octahedral sites (Figure 3.1).^{125,135,143} We infer from previous investigation on multielectron anion redox in LiNaFeS₂ that both Li⁺ and Na⁺ are removed during oxidation,¹²⁵ thereby creating a unique opportunity to explore Li- and Na-based anionic charge compensation in the same material by studying the differences in Li- and Na-discharged LiNaFeS₂ as well as comparing the second cycle of LiNaFeS₂ in both Li and Na cells. Using spectroscopic and structural characterization techniques, we show that despite distinct electrochemical behavior, LiNaFeS₂ undergoes the same redox processes in both cell configurations. We do, however, observe pronounced structural degradation in the Na cell that is not observed when cycling with Li.



Figure 3.1: The crystal structure for LiNaFeS₂ along the (a) bc plane (parallel to c) and (b) ab plane (perpendicular to c). Na and Fe/Li occupy alternating octahedral and tetrahedral layers, respectively.

3.3 Results and Discussion

Structural Characterization

LiNaFeS₂ is prepared as previously reported using solid state synthesis and procured as a metallic dark gray pellet before being ground into a fine black powder.^{125,135} Structural characterization is conducted with synchrotron X-ray diffraction (XRD) and the resulting powder pattern, corresponding Rietveld refinement, and difference curve for as prepared LiNaFeS₂ is shown in the SI (Figure S1). The single-phase fit corresponds to lattice parameters of a = 3.972 Åand c = 6.790 Å. The peaks not described by the fit shown in the Q range of 1.4 Å⁻¹ to 2.3 Å⁻¹ are identical to those seen in Hansen and Zak *et al.*, likely due to superstructure peaks not captured in the $P\bar{3}m1$ model of the LiNaFeS₂ unit cell. The structure of LiNaFeS₂ contrasts with most previously reported Na-Fe-S ternaries in that the FeS₄ tetrahedra are found in 2-D layers. Na₆FeS₄ and Na₅FeS₄ both contain isolated FeS₄ tetrahedra;^{144,145} while Na₃FeS₃ is formed with pairs of edge-sharing FeS₄ tetrahedra¹⁴⁶; and Na₂FeS₂,¹⁴⁷ Na₃Fe₂S₄,¹⁴⁸ and NaFeS₂¹⁴⁹ are reported to have FeS₄ edge-sharing chains.

The materials NaFe_{1.6}S₂ and $[Na_2Fe_3S_4]_{0.5}$ are reported to be isostructural to LiNaFeS₂ with layers of FeS₄ tetrahedra but are not alkali-rich and have not been studied electrochemically.^{150,151} Notably, our previous work determined that the multielectron anion redox observed in LiNaFeS₂ cycled in a Li electrolyte occurs via persulfide bond formation that is likely facilitated by the tilting of corner-sharing FeS₄ tetrahedra after alkali cations have been removed.^{125,135} It is unclear if a similar mechanism would occur in materials with greater Fe occupancy of the tetrahedral layer. Investigating the electrochemical behavior of NaFe_{1.6}S₂ and $[Na_2Fe_3S_4]_{0.5}$ would be informative for the development of Na-ion multi-electron redox sulfides, and the may benefit from the lessons of the present study.

Electrochemical Characterization

LiNaFeS₂ is electrochemically characterized in both Li and Na half cells with Li and Na electrolytes, respectively, to assess differences in redox behavior based on the alkali ion. Both cell set-ups use the corresponding metal foil anode that serves both as the counter electrode (CE) and reference electrode (RE) with a 1 M alkali hexafluorphosphate (PF_6) salt of the respective alkali in a mixture of carbonates (DMC/EC/PC 3/1/1 by volume). The galvanostatic cycling traces for the first and second cycles in both cell configurations are shown in Figure 3.2. Upon charging, LiNaFeS₂ is oxidized and alkali ions are removed. Consequently, a large difference between the Li and Na cells is not expected during oxidation. Indeed, the first charge curves are identical in shape with the exception of small differences at the outset of charging that we attribute to varying initial surface reduction processes at the CE/RE based on the metal foil and electrolyte salt. The first charge is characterized by two different plateau-like regions. The first region encompasses charging to roughly 2.25 V vs. Li or Na corresponding to the removal of approximately 0.65 mol of alkali per formula unit (f.u). A second, more sloping plateau manifests at 2.55 V vs. Li or 2.45 V vs. Na and accounts for an additional 1 e⁻ per f.u. before the material polarizes to the 3 V vs. Li or Na cutoff voltage. The discharge curves mimic those seen previously for Li₂FeS₂ and LiNaFeS₂ in a Li half-cell, and both exhibit one long sloping plateau.^{125,135}

Both cells have disparate first and second charge profiles, suggesting some irreversibility in the first cycle regardless of cell configuration.¹²⁵ During the second charge in the Li cell, the 2.25 V plateau is replaced by a sloping curve and more closely mirrors behavior previously seen in the charging of Li_2FeS_2 .¹²⁵ This change in profile may indicate irreversible redox reactions that could be associated with phase changes or other structural reorganization. The 2.55 V plateau is retained during the second charge, while in the Na half-cell, the second charge profile becomes one continuous sloping region. Irrespective of differences in the shapes of the second galvanostatic cycles, more than one equivalent of e⁻ can be reversibly extracted from both the Li and Na cells. The multielectron behavior continues through the 50th cycle in both cell configurations with the Li cell retaining approximately 0.25 more mol e⁻ reversible capacity (full long-term cycling data can be found in SI Figure S2). In addition, the apparent hysteresis between the charge and discharge curves in the Na cell greatly exceeds that of the Li cell.



Figure 3.2: Galvanostatic cycling of LiNaFeS_2 with a (a) Li anode and LiPF_6 electrolyte and (b) Na anode and NaPF_6 electrolyte at C/10 based on one electron per f.u.

ICP-MS Verification of Mobile Alkali Ion

One origin of disparity between cycling in the two different half cells is the much greater concentration of Li⁺ vs. Na⁺ cations in the electrolytes. Thus, one might expect that the difference in shape observed for the second charge curve could be due to the incorporation of excess Li⁺ or excess Na⁺ compared to the initial LiNaFeS₂ stoichiometry in each respective half cell. In fact, LiNaFeS₂ exhibits multielectron redox in a Li half cell^{125,135} and Na half cell corresponding to the removal of more than one equivalent of alkali ion and implying the mobility of both Li⁺ and Na⁺ in the structure.

To confirm the role of Na in the observed electrochemical differences, inductively coupled plasma mass spectrometry (ICP-MS) is conducted ex-situ on digested cathodes at different states of charge to determine the variation in alkali content over the course of cycling. The results are displayed in Figure 3.3, with the total amount of alkali content as determined by ICP-MS vs. by electrochemistry in addition to the alkali content normalized to the Fe content as ratios of ⁷Li:⁵⁴Fe and ²³Na:⁵⁴Fe. Fe content is expected to remain invariant during cycling. In pristine LiNaFeS₂, the ideal ⁷Li:⁵⁴Fe and ²³Na:⁵⁴Fe ratios are both one and ICP-MS confirms that the pristine material exhibits the expected stoichiometry. Charging corresponds to LiNaFeS₂ oxidation and alkali ion removal, and thus decreases in the ⁷Li:⁵⁴Fe and ²³Na:⁵⁴Fe ratios are expected. After charging to through the first sloping plateau region, both alkali ratios decrease compared to the initial state, with a slightly larger decrease in ⁷Li⁺ content. The Li⁺ and Na⁺ ions in LiNaFeS₂ occupy distinct tetrahedral and octahedral sites, respectively, so these results indicate alkali removal from both layers with a slight preference for removal of Li from the tetrahedral layer at partial charge. Upon full charge, we measure Li⁺ and Na⁺ contents near zero, which aligns well with the electrochemical charge capacity that shows removal of 1.6-1.7 mol e⁻ per f.u. During discharge, both Li⁺ and Na⁺ are re-intercalated into the material with primarily, but not exclusively, reinsertion of the electrolyte ion. The reinsertion of both alkali ions persists to at least the second discharge.

Figure 3.3(d) shows the alkali content in $LiNaFeS_2$ as a function of the electrochemistry when cycled in a Na half cell. The trends are largely the same as those observed in the Li half cell. Both alkali ions are removed after the first plateau, and nearly all the alkali is removed at full charge with a slight residual of Li⁺ left in the material. Upon charge, LiNaFeS₂ again preferentially incorporates the electrolyte cation, Na⁺ in this case, over Li⁺, though 0.5 mol of Li⁺ is reincorporated. We note that approx. 1.5 mol of Na⁺ is measured in the fully discharged LiNaFeS₂, which is greater than the available octahedral sites in LiNaFeS₂. It is unlikely for Na⁺ insertion to occur at the Li tetrahedral sites due to the large size of Na⁺, but the excess Na⁺ may cause nucleation of new, Na-rich phase(s) or be accommodated in distorted or interstitial sites that are not occupied in the initial structure. Na⁺ is found in extremely distorted sites in corrugated layers between metal sulfide layers in the phases Na₂Mn₂S₃ and Na₆In₂S₆.^{152,153} All of these possibilities are likely accompanied by differences in thermodynamic and kinetic barriers which we subsequently evaluate with galvanostatic intermittent titration technique (GITT). These results suggest that the disparate electrochemical behavior of the Li and Na half cells is indeed associated with differences in the mobile alkali ion.



Figure 3.3: Total amount of alkali normalized per formula unit in LiNaFeS₂ cathodes cycled to different states of charge in (a) Li cells acccording to ICP-MS compared with that suggested by electrochemistry with (b) corresponding ratio of alkali to ⁵⁴Fe as determined by ICP-MS of LiNaFeS₂ and (c) corresponding voltage profile. Total amount of alkali normalized per formula unit in LiNaFeS₂ cathodes cycled to different states of charge in (d) Na cells acccording to ICP-MS compared with that suggested by electrochemistry (e) corresponding ratio of alkali to ⁵⁴Fe as determined by ICP-MS of LiNaFeS₂ and (f) corresponding ratio of alkali to ⁵⁴Fe as determined by ICP-MS of LiNaFeS₂ and (f) corresponding voltage profile. Cathodes cycled to different states of charge at C/10 in a (a) Li half cell and (b) Na half cell.

Thermodynamic and Kinetic Overpotentials

We further probe the disparate electrochemical behavior of LiNaFeS_2 in the Li and Na half-cells with GITT experiments. The larger size of the Na⁺ ion compared to that of the Li⁺ ion may affect the kinetic overpotentials during charge and discharge reactions but also the thermodynamic reaction pathways. The less favorable thermodynamics and kinetics of Na⁺ insertion compared to Li⁺ insertion are well-known

in electrochemical separation literature. For example, in FePO₄ the intercalation potentials of Li⁺ and Na⁺ are roughly 0.36 V and 0.19 V, respectively,¹⁵⁴ and the activation barrier of Na⁺ diffusion is 0.05-0.2 eV higher than that of Li⁺. ^{155–157} These lower thermodynamic and kinetic barriers for Li⁺ intercalation can then be leveraged to use FePO₄ for Li⁺ extraction from seawater in spite of extremely low Li⁺:Na⁺ concentration ratios.¹⁵⁸ For our study of LiNaFeS₂, GITT is used to investigate the kinetic overpotentials associated with Li⁺ and Na⁺ removal in both the Li and Na half-cell configurations. GITT is a pulsed current technique that allows for the decoupling of kinetic overpotentials from thermodynamic hysteresis. During the pauses between pulses, the cell is held at open circuit until the voltage relaxes to the near-equilibrium voltage. The overpotential between the voltage of the material under bias vs. that at near-equilibrium can then be attributed to kinetic processes.^{159–162} Locating the near-equilibrium voltages during charge and discharge also enables the decoupling of kinetic overpotentials from thermodynamic hysteresis. From the galvanostatic cycling seen in Figure 3.2 the charge profiles in the Li and Na half-cells exhibit the same behavior during the first cycle and should correspond to the same process, removal of alkali ions and corresponding oxidation of LiNaFeS₂, regardless of the surrounding electrolyte and CE. Therefore, GITT was conducted beginning with the first discharge of each cell configuration, during which differing behavior is expected due to the discrepancy in proportion of reintercalated Li⁺ or Na⁺ observed in ICP-MS.

Figure 3.4(a) shows GITT traces for the first discharge of LiNaFeS₂ in Li and Na half cells. The equilibrium discharge curve can be roughly determined by tracing the points during which no current is passed and those points are plotted in Figure 3.4(b). The equilibrium behavior is very similar regardless of which ion is reinserted. The kinetic overpotential is the difference between the near-equilibrium potential and that during applied bias and is plotted in Figure 3.4(c). In the Li cell, the first discharge corresponds to primarily Li⁺ reinsertion and kinetic overpotentials throughout discharge are relatively constant at ~50-100 mV. The GITT of the preceeding charge, however, has been shown to include a low overpotential region during the initial plateau followed by a higher overpotentials between charge and discharge suggests asymmetric redox processes. For the first discharge of LiNaFeS₂ in the Na half cell the kinetic overpotentials are twice as large as those measured in the Li half cell, ~250 mV, but remain similarly constant throughout discharge. This implies that the kinetic barrier toward Na⁺ reinsertion is much higher than that of

Li.

GITT traces for the second charge in both cell configurations are displayed in Figure 3.4(d) with the near-equilibrium potentials in Figure 3.4e and the overpotentials in Figure 3.4(f). In the Li cell, the second charge GITT trace is very similar to the reported first charge trace, ¹²⁵ with low overpotentials during early states of charge and higher overpotentials during the ~2.5 V plateau. In contrast, the second charge GITT trace in the Na cell is characterized by increasing overpotentials over the course of the charge, reaching as high as 500 mV.

The GITT traces for the second discharge in the Li and Na half cells are shown in Figure 3.4(g) with corresponding near-equilibrium potentials in Figure 3.4(h) and overpotentials in Figure 3.4(i). In the Li cell, the second discharge closely mirrors the first discharge and exhibits similar overpotentials of \sim 50-150 mV with no obvious transition between a region of higher and lower kinetic barriers. For the Na cell, the shape of the second discharge is similar to that of the first discharge but accompanied by greater overpotentials, indicating that the second charge process involves irreversible changes in the material.

Figure 3.4(e) also shows the thermodynamic hysteresis, i.e. the difference in the near-equilibrium potentials of the second charge and second discharge curve, as shaded regions. The thermodynamic hysteresis is actually quite similar for both cell configurations in a range of 200-300 mV, although the equilibrium charge and discharge curves for the Li cell retain flatter slopes than those for the Na cells. These results point to the kinetics of Na⁺ diffusion as the primary challenge for the application of LiNaFeS₂ as a Na cathode.

Characterization of Redox Processes

Previous work in a Li half-cell employed Fe and S K-edge X-ray absorption spectroscopy (XAS) to investigate the nature of the multielectron redox charge compensation in LiNaFeS₂. Based on those measurements, initial charge to 2.5 V vs. Li was assigned to Fe-based charge compensation, followed by S-based anion oxidation to form persulfides when charging further to 3 V vs. Li.¹²⁵ To determine whether the excess capacity obtained when cycling LiNaFeS₂ in Na cells originates from the same processes as in Li cells, we conduct Fe and S K-edge XAS studies on *ex-situ* samples prepared from LiNaFeS₂ cathodes cycled to five states of charge in both cell configurations.

First, we discuss the Fe K-edge XAS data that is shown in Figure 3.5. The Fe K-edge



Figure 3.4: (a) GITT curves of the first discharge of $LiNaFeS_2$ in Li and Na half cells. The cell is polarized at C/10 for 20 m with 4 h intermittent rest periods at OCV. The (b) corresponding equilibrium potentials, and (c) calculated overpotentials the first discharge. (d) GITT curves of the second charge of $LiNaFeS_2$ cycled in Li and Na half cells. The (e) corresponding equilibrium potentials and (f) calculated overpotentials the second charge. Panel (e) shows the thermodyanmic hysteresis of the second cycle for each cell as shaded regions. (g) GITT curves of the second discharge of $LiNaFeS_2$ cycled in Li and Na half cells. The (b) corresponding equilibrium potentials the second charge of LiNaFeS cycled in Li and Na half cells. The (c) corresponding equilibrium potentials curves of the second cycle for each cell as shaded regions. (g) GITT curves of the second discharge of $LiNaFeS_2$ cycled in Li and Na half cells. The (h) corresponding equilibrium potentials and (i) calculated overpotentials the second discharge.

XAS has two main features: the pre-edge feature that arises from spin-forbidden transitions between the ground state and mixed metal 3d and ligand 3p states and the rising edge that corresponds to electronic transitions between the ground state and 4p states.^{163–165} The pre-edge intensity is affected by metal-ligand covalency and degree of mixed d/p band occupation, but is also sensitive to atom coordination geometry. The rising edge is frequently used as a proxy for metal oxidation state and its position can be identified as the local maximum of the first derivative of the absorption spectrum. The first derivatives are shown in Figure 3.5 to aid in discerning the rising edge position.

The spectrum of pristine LiNaFeS₂ is shown in Figure 3.5(a) and is characterized by a pre-edge feature at 7112.6 eV with a rising edge position of 7117.2 eV. This corresponds well with previously reported spectra of LiNaFeS₂.¹²⁵ The spectrum of the pristine material is duplicated in subsequent panels to aid comparison. The corresponding first derivative is shown in Figure 3.5(b), and this is also replicated in subsequent panels. Figure 3.5(c) shows the spectra of pristine LiNaFeS₂ overlaid with spectra of LiNaFeS₂ charged to ~2.5 V vs. the respective RE in Li and Na half cells. The spectra of LiNaFeS₂ partially charged in Li and Na cells are nearly identical, with both exhibiting a pre-edge shift of ~0.7 eV to 7113.3 eV. The rising edge positions for both samples also shift by approximately 1 eV to 7118.2 eV, which is easily observed in the first derivative in Figure 3.5(d). A positive shift in the Fe K-edge position typically indicates Fe²⁺ oxidation to Fe^{2+/3+}, and previous work on $[L_2Fe_2S_2]^n$ compounds observed pre-edge positions of 7112.1 eV and 7113.0 eV and rising edge positions of 7117.4 eV to 7118.3 eV during oxidation from Fe²⁺-Fe²⁺ to Fe^{2+/3+}-Fe³⁺ species, respectively.¹⁶³

The fully charged Fe K-edge spectra for both the Li and Na cells (Figure 3.5(e)) are also extremely similar both in shape and position. Compared to the spectra measured at partial charge (~ 2.5 V), the pre-edge features are slightly broader and more intense and the post-edge peak is slightly higher in intensity. The increasing pre-edge intensity with charge suggests an increasingly covalent Fe *3d*-S *3p* interaction or an increasingly distorted Fe coordination polyhedron. The first derivative shown in Figure 3.5(f) shows that the edge position does not shift between 2.5 V to full charge for either cell configuration, corroborating the previous report of Fe-based charge compensation at the beginning of charge and Fe redox inactivity when charging past ~ 2.5 V.¹²⁵

During the subsequent discharge, the Fe K-edge position shifts back to 7117.2 eV and the pre-edge position shifts back to 7112.9 eV when cycled in the Li and Na half cells (Figure 3.5(g)). This reflects highly reversible transition metal redox, although the discrepancy in pre-edge position and intensity may indicate that the local Fe coordination environment is altered after the first cycle. In fact, the shape of the Fe K-edge XAS spectra is slightly different when the LiNaFeS₂ is cycled in the Li half cell vs. the Na half cell. Thus, the excess Na incorporated is changing the structure but not the charge compensation mechanism. The edge shift is easily observed in the first derivative plot in Figure 3.5(h). After the second charge, the Fe K-edge absorption spectra of both Li- and Na-cycled LiNaFeS₂ are nearly identical to those of the first full charge with similarly broadened and intense pre-edges at 7113.3 eV and rising edge positions at 7118.2 eV (Figure 3.5(i)). The spectra of the material after second discharge overlay similarly to the spectra of the first discharge, with again slight differences in shape. The pre-edge intensities of the first and second discharge samples in the Fe K-edge absorption spectra appear slightly higher in the Li-cycled samples than the Na-cycled samples, but the implications are inconclusive given the minimal difference and insensitivity of the Fe pre-edge. The oxidation is again reversible, with the position of the rising edge in the spectra of the materials discharged on the second cycle shifting back to that of the pristine material (Figure 3.5(j) and (k)).

To identify the role of anion redox in the multielectron processes occurring during LiNaFeS₂ cycling, S K-edge XAS is measured ex situ at various states of charge. The regions of S K-edge XAS have the same band origins as those in the Fe Kedge spectra, but arise from the 1s ground state of S rather than Fe (pre-edge and edge corresponding to the S $1s \rightarrow$ Fe 3d/S 3p and S $1s \rightarrow$ S 4p electronic transitions, respectively).^{163,164} As such, the pre-edge transition is no longer spin-forbidden and its intensity is a more direct probe of the metal-ligand covalency. The S K-edge absorption spectra are depicted in Figure 3.6 with a reference spectrum for FeS₂ shown in panel (a). In FeS₂, all S is present as persulfides (S_2^{2-}) , which manifests as a large pre-edge feature at roughly 2471.4 eV corresponding to the transition from the S 1s ground state to the unoccupied antibonding S 3p states, or a σ^* band, generated from S-S bond formation.¹⁶⁶ The position of the FeS₂ pre-edge is highlighted with a shaded region in panels (b)-(f) and the spectrum of the pristine material is reproduced in each panel, as well, for ease of comparison. The pristine LiNaFeS₂ spectrum exhibits a pre-edge feature at 2470.0 eV followed by a rising edge. The significant overlap between the pre-edge peak and rising edge complicates the identification of the rising edge position and cannot be accomplished without principal component analysis, and as such our discussion of the S K-edge absorption spectra is limited to the pre-edge position, relative shifts in the rising edge, and qualitative shape of the spectra.

The S K-edge spectra of LiNaFeS₂ after charging to 2.5 V in both the Li and the Na half cell are shown in Figure 3.6(b). Charging to ~2.5 V in either cell configuration results in a significant increase in pre-edge intensity and slight shift to a lower energy of 2469.7 eV. The simultaneous increase in the S K-edge and Fe K-edge pre-edge intensities provide strong evidence for increasing Fe-S covalency arising from the initial oxidation of Fe²⁺ to Fe^{2+/3+}. The S K-edge spectra of LiNaFeS₂ after the first charge in both the Li and the Na half cell are shown in Figure 3.6(c). Upon fully charging LiNaFeS₂ to 3 V, the 2470.0 eV pre-edge feature decreases in intensity and a new pre-edge feature appears at 2472.7 eV. This new pre-edge feature falls within the range of the FeS₂ pre-edge and is attributed to an electronic transition

to the σ^* band that arises due to persulfide formation.¹²⁵ Concurrently, the rising edge also shifts to higher energies confirming S oxidation. The S K-edge spectra of LiNaFeS₂ after the first discharge in both the Li and the Na half cell are shown in Figure 3.6(d). Both spectra obtained after discharging in Li and Na half cells overlay nearly perfectly with that of pristine LiNaFeS₂ with the exception of slightly higher pre-edge intensity, which was also observed in the Fe K-edge absorption spectra. The discrepancy between the pre-edge positions of the discharged samples and that of the pristine is at most 0.1 eV, which is within the margin of the S K-edge spectral resolution. The second charge and discharge S K-edge spectra seen in Figure 3.6(e-f) mirror the behavior of the first charge and discharge, confirming that the persulfide formation is reversible. While both the Li- and Na-cycled LiNaFeS₂ spectra are nearly identical at the states of charge characterized, the spectra of the LiNaFeS₂ after first and second discharge in the Na half cell show slightly higher pre-edge intensities than their Li-cycled counterparts. This corresponds to a greater probability of the S $1s \rightarrow \text{Fe} 3d/\text{S} 3p$ electronic transition which could indicate a more distorted S coordination geometry to accommodate the movement of the larger Na ion.



Figure 3.5: The Fe K-edge XAS and the associated first derivative for (a, b) pristine $LiNaFeS_2$. *Ex-situ* Fe K-edge XAS of $LiNaFeS_2$ cycled in Li and Na half cells after (c, d) charging to 2.5 V, (e, f) full charge, (g, h) first discharge, (i, j) second charge, and (k, l) second discharge. All cells were cycled at C/10 based on one electron per f.u. The Fe K-edge position of pristine $LiNaFeS_2$ is marked by the dashed gray line. The pristine spectrum and its derivative are reproduced in each panel in black.



Figure 3.6: (a) S K-edge XAS of pristine LiNaFeS₂ with a reference spectrum of FeS₂. *Ex-situ* S K-edge XAS of LiNaFeS₂ cycled in Li and Na half cells to (b) 2.5 V during the first charge, (c) full first charge, (d) first discharge, (e) second charge, and (f) second discharge. All cells were cycled at C/10 based on one electron per f.u. The pristine spectrum is reproduced in each panel in black and the pristine and FeS₂ pre-edge positions are marked with a black dashed line and solid dark gray line, respectively. The approximate position of the pre-edge of FeS₂ is shown as a shaded region in each panel.

Ex-situ Structural Characterization

The characterization of the electronic structures in Li and Na cells revealed subtle differences, but appear insufficient to explain the large discrepancies observed in the electrochemistry. The changes in the profiles could also be due to the difference in chemical potential of the mobile ion and/or different structural responses. Though the effect of the mobile ion is difficult to probe quantitatively, we can probe the structural response upon redox.

In previous work, Hansen and Zak *et al.* performed *operando* XRD on LiNaFeS₂ cathodes in Li half cells and followed the evolution of the (001) reflection. During charging up to 2.5 V vs. Li corresponding to Fe oxidation, a second reflection (001) reflection grows in and is ascribed to the appearance of a new phase.¹²⁵ This supports the idea of a two-phase transition occurring during the initial portion of the

first charge. Charging beyond 2.5 V leads to a continuous increase in the reflection more akin to a solid solution mechanism. In this study, we aim to probe potential differences in structural changes during cycling for LiNaFeS₂ in both Li and Na half cells using synchrotron XRD by analyzing *ex-situ* samples taken at various states of charge during the first two cycles.



Figure 3.7: Synchrotron *ex-situ* XRD in the 0.7 to 4 Q range of LiNaFeS₂ cathodes cycled at C/10 in Li and Na half cells after (a) no cycling (pristine), (b) 1st plateau, (c) 1st charge, and (d) 1st discharge.

The *ex situ* synchrotron XRD of LiNaFeS₂ cycled in both the Li and Na half cells at various states of charge in the first cycle are shown in Figure 3.7. In the Li half cell, charging to the end of the first plateau to 2.55 V results in broadening of all reflections present in the pristine pattern, and the (001) reflection shifts to a higher Q-value corresponding with the removal of alkali ions and consequent contraction of the lattice along the c-axis. Peak broadening in XRD indicates loss of crystallinity. New peaks manifest at Q = 1.25 Å⁻¹, between the (012) and (003) reflections of



Figure 3.8: Synchrotron *ex-situ* XRD in the 0.7 to 4 Q range of LiNaFeS₂ cathodes cycled at C/10 in Li and Na half cells after (a) no cycling (pristine), (b) 2nd plateau, (c) 2nd charge, and (d) 2nd discharge.

the pristine material, as well as to the right of the (011) peak. This corroborates the two-phase mechanism in this region reported by Hansen and Zak *et al.*¹²⁵ In the diffraction of LiNaFeS₂ cycled to 2.5 V in the Na half cell, no significant differences are observed compared to the Li half cell which again confirms that the first charge mechanism is similar in both configurations.

Further charging to 3.0 V in both cells causes a shift of the (001) reflection to higher Q, consistent with continued lattice contraction during oxidation and alkali de-intercalaion, and several reflections disappear including the reflection near 1.25 Å⁻¹ and those observed in the Q range of 1-1.9 Å⁻¹. The phase present at the end of charge is the same in both cells and does not correspond to any reported phases to the best of our knowledge including pyrite and marcasite FeS₂,^{167,168} FeS,¹⁶⁹ and NaFeS₂.¹⁴⁹ The reflections are either broadened and shifted reflections of the

pristine phase or arise due to the two-phase nature of the oxidation.

After the first discharge in both the Li and Na half cells, all reflections have broadened significantly compared to the pristine cathode material. The (001) reflection shifts back to lower Q, although the LiNaFeS₂ discharged in the Li half cell does not completely recover the position in the pristine state. This aligns with previous XRD measurements from Hansen and Zak *et al.*, and we can now confirm it results from the re-insertion of the smaller Li⁺ in the octahedral layer in place of the initial Na⁺. The complete recovery of the pristine (001) reflection position in the Na-discharged sample is also consistent with occupation of the octahedral layer with re-inserted Na⁺. All reflections seen in the discharged samples are also observed in the pristine LiNaFeS₂ cathode with the exception of a broadening between the (100) and (001) reflection in the discharged state, potentially due to formation of a Li₂FeS₂ phase in conjunction with an expanded LiNaFeS₂ phase.

The *ex situ* synchrotron XRD of LiNaFeS₂ cycled in both the Li and Na half cells at various states of charge in the second cycle are shown in Figure 3.8. During the second charge to 2.55 V in the Li cell, the same positive shift of the (001) reflection seen in the first charge to 2.55 V is observed, but the overall pattern shows significantly less two-phase behavior than in the first cycle. This correlates well with the more sloping appearance of the second galvanostatic charge curve. In the Na cell, a positive (001) shift is also seen, but the material appears to undergo significant amorphization with significant broadening. This obscures the exact positions of most reflections and prevents further conclusions from being drawn about the mechanism during second charge with Na. Further charging to 3.0 V in the Li cell again yields a different phase with a more contracted lattice as evidenced by a continued positive shift of the (001) reflection. The diffraction pattern of LiNaFeS₂ at the end of second charge in an Li cell appears identical to that from the first charge, whereas the end of second charge pattern.

After the second discharge in the Li half cell, the diffraction pattern is identical to that of the first discharge, including the broadened area between the (100) and (001) reflections. This confirms that LiNaFeS₂ cycling in a Li half cell is structurally reversible after an irreversible change during the first charge process. The XRD pattern measured on LiNaFeS₂ cycled to the second discharge in the Na half cell, however, shows minimal intensity for any reflection indicating significant structural

amorphization with very few discernible peaks. The level of amorphization after cycling in the Na half cells is indicative of larger structural issues during cycling. The ability of Na⁺ to support both octahedral and prismatic coordination has been associated in other materials with electrochemical creep during cycling that leads to degradation in overall performance. A shift in coordination from octahedral to prismatic generally occurs at low degrees of alkalation as the greater Na-*X* (where *X* is an anion) distance of the prismatic coordination becomes favorable to reduce repulsion between the transition metal chalcogenide (MX_2) layers. The mechanism of this coordination change during charge is a shift in the stacking sequence of the MX_2 layers that is path independent from the shift back during discharge, leading to layer shearing and visible particle exfoliation.^{93,170–173} Notably, cracking in LiNaFeS₂ has also been previously observed when cycled in Li half cells and was cited as one of the factors responsible for accelerated capacity fade.¹³⁵

Consequently, scanning electron microscopy (SEM) is used to evaluate the structural degradation. Energy dispersive spectroscopy (EDS) is also employed to identify regions with high Fe and S content (see SI Figures S4-6) to differentiate LiNaFeS₂ particles from the surrounding cathode matrix. Individual LiNaFeS2 particles are then examined for signs of structural damage. SEM of $LiNaFeS_2$ particles in the pristine state and after the first discharge in the Li and Na half cells are shown in Figure 3.9. Pristine LiNaFeS₂ has an obvious layered morphology with particles that are plate-like and show parallel striations that likely align with the ab plane. Figure 3.9(b) shows a particle of LiNaFeS₂ after discharging in a Li half cell. The striations in the particles are exacerbated compared to the pristine material and appear as cracks, but are still manifested as thin, distinct, straight lines. Figure 3.9(c) shows a particle of LiNaFeS₂ after discharging in a Na half cell. The particle appears severely roughened with much different morphology compared to that discharged in the Li half cell. The particle morphology of the Na-discharged sample is also significantly rougher than particles of Li-discharged LiNaFeS₂ imaged in previous work from Kim et al. with transmission X-ray microscopy (TXM).¹³⁵ Thus, the incorporate of the larger Na⁺ causes significant structural changes not only on the atomic scale, but also on the micron scale.

Capacitive Contributions in LiNaFeS₂ Cycling

When particles roughen, the surface area increases which can lead to an increase in capacitance. To further probe the nature of the observed particle roughening, b-value analysis is conducted on LiNaFeS₂ cathodes after one cycle (charge and



Figure 3.9: *Ex-situ* SEM images of LiNaFeS₂ cathodes in the (a) pristine state and discharged at C/10 in a (b) Li half cell to 1.7 V vs. Li and in a (c) Na half cell to 1.1 V vs. Na.

discharge) in Li half cells vs. Na half cells to compare the capacitive contributions. The *b*-value is derived from the power-law relationship between the sweep rate (v) and the current response *i* in a cyclic voltammetry (CV) experiment¹⁷⁴:

$$i(v) = av^b \tag{3.1}$$

where a and b are constants. By taking the logarithm of both sides of (3.1), we then obtain:

$$log(i(v)) = b \cdot log(a) + b \cdot log(v)$$
(3.2)

and from this relation, we can construct log-log plots of the peak current vs. scan rate to extract the *b*-value as the slope. For capacitive charge storage, peak current varies linearly with scan rate $(i_p \sim v^1)$:

$$i_p = vCA \tag{3.3}$$

where *C* is capacitance and *A* is the surface area of the electrode.

In contrast, Faradaic processes are limited by semi-infinite diffusion and consequently the peak current varies with the square root of the scan rate $(i_p \sim v^{1/2})$ following the Randles-Sevcik equation:¹⁷⁵

$$i_p = 0.4463nFAcD^{1/2}v^{1/2}(\frac{\alpha nF}{RT})^{1/2}$$
(3.4)

where *n* it the number of electrons transferred, *c* is the surface concentration of the redox active material, α is the transfer coefficient, *D* is the diffusion coeffcient, *A* is the electrode surface area of the electrode, *R* is the ideal gas constant, and *T* is temperature.

Therefore, the *b*-value can then be used to evaluate the relative capacitive and Faradaic contributions. Capacitive and Faradaic processes result in *b*-values of 1.0 and 0.5, respectively.^{176–178} Figure 3.10 shows CVs of LiNaFeS₂ measured at different scan rates after one cycle (charge then discharge) in Li and Na half cells. Each trace is measured on a new, freshly discharged cathode. The current is normalized by active material mass, and $log(i_p)$ at each scan rate during the cathodic scan is plotted against log(v) in Figure 3.10 (c) and (d) along with the lines of best fit, R² values and *b*-values. Voltammetry of LiNaFeS₂ after one cycle in the Li half cell shows the particles have a *b*-value of 0.788, which corresponds with the behavior expected from mixed Faradaic processes associated with intercalation and deintercalation and capacitive contributions. Voltammetry of LiNaFeS₂ after one cycle in the Na half cell, however, reveals a much higher *b*-value of 0.961, indicating much more capacitive contributions. These results support the conclusion that after discharging in Na half cells, the LiNaFeS₂ particles are rougher due to particle fracturing compared to discharging in Li half cells.

Discussion of Observed Cycling Differences Between Li and Na Half-Cells

Regardless of cell configuration, the first charge of LiNaFeS₂ exhibits two plateaus. Hansen and Zak *et al.* used a combination of Fe- and S- K-edge XAS to assign the first charge region to $Fe^{2+/3+}$ and the second to anion redox with persulfide formation,



Figure 3.10: Cyclic voltammograms of LiNaFeS₂ that is first discharged at C/10 in (a) Li and (b) Na half cells. Scan rates range from 0.025, 0.05, 1.0, 2.0, and 3.0 mV s⁻¹ and each CV is measured on a freshly discharged electrode. The corresponding log-log plots for b-value determination for LiNaFeS₂ cycled in the (c) Li and (d) Na half cells.

 S^2 -/ S_2^{2-} , ¹²⁵ and these results are confirmed again here. Upon the first discharge, however, the majority carrier in the electrolyte is preferentially reintroduced due to the much higher activity of that carrier in the electrolyte. The different alkali content causes the subsequent charge mechanism to diverge, allowing for a comparison between Li- and Na-related processes. The shapes of the cycle 2 galvanostatic curves differ with the curves measured in the Li half cell retaining the two plateau character while the curves measured in the Na half cell become more sloping. The difference in curves shape is correlated with the different structural response associated with incorporating the large Na⁺, which causes amorphization of the material.

We note that in Na-containing materials, a smooth, sloping galvanostatic profile has been correlated to prismatically coordinated Na.^{179,180} However, prismatic coordination alone is insufficient to explain the observed electrochemistry of LiNaFeS₂ cycled in a Na half cell, as prismatically coordinated Na frequently results in fast diffusion kinetics and smaller ($\leq 100 \text{ mV}$) overpotentials observed in GITT.^{180–182} In the case of LiNaFeS₂, the larger contributions of Na⁺ incorporation and removal in the Na half cell result in much larger overpotentials.

Interestingly, from an electronic structure perspective, we show that the charge compensation mechanisms between LiNaFeS_2 cycled in a Li vs. Na half cell is very similar, if not identical. Subtle differences in the Fe K-edge and S K-edge absorption spectra suggest slight differences in atom coordination environments. Overall, spectroscopic characterization does not account for the disparate electrochemical behavior seen between LiNaFeS₂ in Li and Na half cells.

However, the difference in the structural responses to Li vs. Na re-insertion after first charge is very different which could be a driving factor for the differences in electrochemistry. We note that the chemical potential of the mobile ion will also play a role in dictating the voltage curves. ICP-MS measurements show that more Na⁺ is re-inserted than there are available octahedral sites in the initial pristine structure, which could indicate that the Na-discharged LiNaFeS₂ accommodates Na through the nucleation of a more Na-rich phase such as $Na_3Fe_2S_4$ or Na_2FeS_2 , ^{147,148} distortion of the structure with intercalation into previously unoccupied sites, or adsorption of Na as opposed to intercalation. We anticipate that the nucleation of new phases or significant structural distortion should be apparent in the XRD patterns of cycled LiNaFeS₂ material. However, no new reflections are observed in the Na-discharged cell compared with the Li-discharged cell, which makes the probability of significant new phase nucleation unlikely. The phase could be poorly crystalline, however, making it difficult to detect with XRD. Instead, the ex-situ XRD show evidence of severe amorphization in the Na cells, which is correlated with particle exfoliation and roughening that is visible in SEM. Particle exfoliation and roughening are well-known phenomena in Na cathode materials frequently attributed to destructive phase transitions during cycling that are supported by Na's propensity to stabilize in both octahedral and prismatic coordinations. 170,171

Phase transitions driven by Na⁺ converting from an octahedral to prismatic coordination are typically visible by the appearance of a second (001) reflection at higher Q values due to a glide transition, ¹⁷³ and it is possible that such a change in coordination is responsible for the two phases observed when charging the Li and Na cells to the first 2.5 V plateau. Additionally, that two-phase mechanism disappears in the second charge in the Li cell when very little Na is present during cycling, although the extent of pattern broadening makes it difficult to determine if the mechanism is still present during the second charge in the Na cell. Regardless, while an octahedral to prismatic phase transition frequently leads to particle cracking, it is not necessarily associated with the levels of amorphization or electrochemical charge smoothing we observe and can in fact be reversible while preserving material crystallinity and distinct electrochemical signatures of two-phase behavior.^{173,183,184} This implies that the excess Na⁺ re-inserted in previously unoccupied sites during discharge plays a more significant role in the amorphization. In fact, particle roughening due to cycling with a Na electrolyte is confirmed with imaging and electrochemical analysis. Altogether these results paint a complex picture of the structural changes that can be incurred in Na-cycled LiNaFeS₂ in spite of reversible changes in the electronic structure that are identical to those observed when cycled in a Li half cell.

3.4 Conclusions

The mixed alkali nature of LiNaFeS₂ allows for cycling in both Li and Na half cells, which enables a direct comparison of Li- and Na-related processes in a similar material. Indeed, LiNaFeS₂ is capable of reversible multielectron anion redox in a Na half cell. After the first discharge, the electrochemical traces of LiNaFeS₂ differ depending on the electrolyte composition which is correlated to preferential incorporation of the electrolyte cation. Although cycling LiNaFeS₂ in a Na cell does not result in significant changes in the Fe or S K-edge XAS data compared to the Li cell, it does incur prominent structural differences as evidenced by amorphization and particle roughening observed with synchrotron XRD, SEM, and cyclic voltammetry. These structural changes are also associated with larger kinetic overpotentials that we attribute to sluggish movement of the bulky Na⁺ through heavily fractured cathode particles.

Overall, we show that for LiNaFeS₂ the anion redox mechanism is unaffected by the mobile alkali ion. This contrasts with previously observed differences in the accessible anion redox capacity in Li_2TiS_3 vs. Na_2TiS_3 ,¹⁴⁰ though we note that the proposed mechanisms of anion redox differ–FeS₄ tetrahedral tilting in LiNaFeS₂ compared with overall S lattice distortion in Na_2TiS_3 . Based on this study the primary challenge in development of Na anion-redox cathode materials appears to be developing methods to stabilize structures during the disruptive cycling of the large Na⁺, the same as in other Na layered transition metal chalcogenides.

3.5 Experimental

Materials Preparation All materials were prepared in an Ar-filled glovebox in which O_2 and H_2O levels were <1 ppm. LiNaFeS₂ was prepared using solid state synthesis methods adapted from the previously reported by Hansen and Zak *et al.*, from Li₂S (Thermo Scientific 99.9%), Na₂S (Thermo Scientific), Fe (Acros Organics, 99.0%), and S₈ (Acros Organics, >99.5%). Stoichiometric powders of Li₂S, Na₂S, Fe, and S₈ were ground in a mortar and pestle and pressed into pellets of up to 500 mg and sealed in evacuated vitreous silica ampules. Carbon coating did not affect the reaction. Reactants were heated at 2°C min⁻¹ to 500-600°C with a dwell time of 96 h before cooling to room temperature. The resulting black pellet was ground into a powder in the glovebox for further characterization.

Electrochemical Testing Electrodes were prepared in an Ar-filled glovebox as freestanding electrodes. A 50/40/10 (wt %) mixture of active material, conductive carbon (SuperP, Alfa Aesar, >99%), and PTFE binder (Sigma, 1 µm powder), respectively, was combined in an agate mortar and pestle and hand ground for five minutes in batches of 30-100 mg total. The powder was then pressed into 3/8 in. diameter electrodes by hand to yield electrodes of 7-15 mg (total). All electrochemical cells were assembled inside an Ar-filled glovebox (H₂O and O₂) <1 ppm). All electrochemistry for spectroscopic characterization was performed in 2032 coin cells (MTI) with a stainless steel spring (MTI), stainless steel spacer (MTI), metal foil anode, glass fiber separator, 160-200 μ L of electrolyte, and a working electrode of 50 wt % active material as previously described. Li-foil anodes with 1/2 in. diameters were punched from Li ribbon (Sigma, 99.9%, 0.75 mm) that was mechanically cleaned with an Xacto blade immediately prior to cell assembly. To produce Na foil anodes, the oxidized ends of Na sticks (Thermo Scientific 99.8%) were cut off with an Xacto blade and an appropriately sized chunk of fresh metal was sliced and rolled into a thin foil between two sheets of polypropylene (Celgard 2400) with a pasta roller prior to punching into 1/2 in. diameter disks. Electrolyte was prepared as 1 M solutions of LiPF₆ (Oakwood Chemical, Battery grade) or NaPF₆ (Beantown Chemical, 99%) in a 3/1/1 (by volume) mixture of dimethyl carbonate (DMC), ethylene carbonate (EC), and propylene carbonate (PC) (all Sigma,≥99%). Electrolytes were prepared in dried HDPE bottles by combining the salt and carbonate mixtures and allowing to dissolve and homogenize overnight prior to use. LiNaFeS₂ was charged (oxidized) at a C/10 rate based on 1 e⁻ per

formula unit to 3 V and discharged at the same rate to 1.7 V in the Li cells and 1.1 V in the Na cells. For some *ex-situ* samples, a lower oxidation cutoff potential of 2.5 V was used. Voltages are vs a Li or Na metal anode as indicated, which are assumed to be at the Li/Li⁺ or Na/Na⁺ reference potentials, respectively. Electrochemical experiments were performed with a VMP3 multichannel potentiostat (Bio-Logic) or BCS 805 battery cycler (Bio-Logic). For GITT experiments, currents were applied at a C/10 rate based on 1 e⁻ per formula unit separated by 4 h rest periods.

Structural Characterization High-resolution synchrotron powder X-ray diffraction (XRD) patterns were collected on samples sealed under vacuum in 1.0 mm (o.d) glass capillaries (to prevent air exposure) or samples packed in 0.5 mm (o.d) quartz capillaries and sealed with epoxy (Torr Seal) and placed inside polyimide capillaries. To examine structural changes at different states of charge, 2032 coin cells with freestanding electrodes prepared without binder were used. The remaining components of coin cell assembly were as previously described. The electrode composition for these experiments was 60/40 (wt %) active material and conductive carbon (SuperP, Alfa Aesar, >99%) which was hand ground for five minutes in an agate mortar and pestle prior to hand pressing to 3/8 in. diameter electrodes with a stainless steel die set. Total electrode masses were 8-12 mg. The electrodes were cycled to the desired voltage cutoffs (pristine, charged to 2.5 V, charged to 3 V, discharged to 1.7 or 1.1 V based on cell set-up, second charge to 2.5 V, second charge to 3 V, and second discharge to 1.7 or 1.1 V) and disassembled. After disassembly any visibly remaining GFD was manually scraped off the cathode surface, and the cathodes were subsequently washed with DMC and dried under vacuum at 60°C for 6 h. The dried cathodes were crushed into fine powders before being loaded into the XRD capillaries. Samples were measured on beamline 28-ID-1 ($\lambda = 0.1665$ Å) at the National Synchrotron Light Source II at Brookhaven National Laboratory. The diffraction patterns were fit with the Rietveld method using the General Structure Analysis System II (GSAS-II),¹⁸⁵ and visualization of the crystal structures was aided by VESTA.¹⁸⁶

ICP-MS Inductively coupled plasma mass spectrometry (ICP-MS) was conducted at the Resnick Environmental Analysis Center at Caltech with an Agilent 8800 ICP-MS and argon plasma source. *Ex-situ* samples were prepared by cycling 2032 coin cells assembled as described in the electrochemical testing section to desired voltage cutoffs (pristine, charged to 2.5 V, charged to 3 V, discharged to 1.7 or 1.1 V based on cell set-up, second charge to 2.5 V, second charge to 3 V, and second discharge to 1.7 or 1.1 V) followed by cell disassembly. After disassembly any visibly remaining GFD was manually scraped off the cathode surface, and the cathodes were subsequently washed with DMC and dried under vacuum at 60°C for 6 h. Samples were diluted to concentrations of 21.3 μ M LiNaFeS₂ by first digesting approximately 0.2 mg of *ex-situ* material in 2-3 mL of concentrated HNO₃ (70 vol %) followed by sequential dilutions with dilute HNO₃ (5 vol%). Final sample volumes were 25 mL. Standard solutions were prepared by diluting stock solutions of Li, Na and Fe to the desired concentrations with dilute HNO₃ (5 vol%). Exact concentrations for the different standards can be found in the SI.

Spectroscopic Characterization Samples for *ex-situ* X-ray absorption spectrosopy (XAS) were prepared in 2032 coin cells as previously described for electrochemical experiments. The cells were cycled to the desired voltage cutoffs (pristine, charged to 2.5 V, charged to 3 V, discharged to 1.7 or 1.1 V based on cell set-up, second charge to 3 V, and second discharge to 1.7 or 1.1 V) and disassembled. After disassembly any visibly remaining GFD was manually scraped off the cathode surface, and the cathodes were subsequently washed with DMC and dried under vacuum at 60°C for 6 h. The dried cathodes were then crushed into fine powders. Fe K-edge XAS was measured at beamline 4-3 at the Stanford Synchrotron Radiation Lightsource at SLAC National Accelerator Laboratory. For analysis, the dried powders were directly loaded into stainless steel holders provided by beamline 4-3 with Kapton tape on either side. Fe K-edge data were calibrated to a collinear Fe foil present for each sample.

S K-edge XAS was conducted at beamline 8-BM at the National Synchrotron Light Source II at Brookhaven National Laboratory. Data processing including calibration and background correction was performed using Athena.¹⁸⁷ The S K-edge data were calibrated to a gypsum standard (1 wt% $CaSO_4*2H_2O$ in polyethylene glycol). *Ex situ* samples were prepared by grinding cycled cathode material with boron nitride to achieve 5 wt% S concentrations. Pellets were then sandwiched between a polypropylene layer and Kapton tape and adhered to the sample holder using Kapton tape. All sample preparation was conducted inside an Ar-filled glovebox. During measurement, the sample holder was placed in a continuous He-flushed chamber to minimize air exposure. Each scan lasted about 15 minutes, and 3 scans were averaged.

3.6 Acknowledgements

This work was funded by the Office of Naval Research Young Investigator Award, award no. N00014-22-1-2329. M.D.Q., E.S.P., and C.T.M. acknowledge support from the National Science Foundation Graduate Research Fellowship under grant no. 2139433.
Chapter 4

VACANCIES IN THE TRANSITION METAL LAYER UNLOCK REDOX IN NACU_{1.5}FE_{0.5}S₂

[This chapter is temporarily embargoed]

Chapter 5

FUTURE OUTLOOK

In Chapter 2, we discussed S_8 addition as a method to control polysulfide equilibria and slow Mg anode passivation. This method lacks practicality in a closed cell, but could potentially be useful in a more open systems such as a flow battery. Although our work increases our fundamental chemical understanding of the Mg-S system, the realization of Mg-S batteries likely requires at least one of three things: engineering measures to prevent the shuttling of polysulfides to the Mg anode such as architectured separators or cathodes, an artificial solid-electrolyte interphase that can protect the Mg anode from passivation while still permitting the plating and stripping of Mg²⁺, or electrolyte design that minimizes polysulfide solubility while maintaining acceptable Mg²⁺ mobility.^{188–190} Work in all of these areas is ongoing within the field, but separate from the polysulfide conundrum is the sensitivity of the Mg anode to passivation in common electrolyte solvents. Research in the areas outlined above has already advanced significantly in Li-S systems, to the point where several companies are seeking to eventually commercialize Li-S batteries.¹⁹¹ Many of the strategies for preventing polysulfide dissolution and shuttling may be the same between the Li-S and Mg-S systems, but Mg-S batteries will also require discovery of novel electrolytes that promote facile Mg²⁺ plating and stripping.

In the design of batteries with metal anodes, the interface between the metal and electrolyte is essential towards proper functioning. The high reducing power of Li and Mg metal results in the formation of a solid-electrolyte interphase (SEI)–a film between the pure metal anode and surrounding electrolyte. In order for effective metal plating and stripping to take place, the SEI must be ionically conductive while also being electronically insulating to prevent continued reaction with the electrolyte. While these properties hold for most SEIs on Li metal, the same is not true for Mg.^{192,193}

A variety of classes of Mg electrolytes have been developed including Grignardbased, ¹⁹⁴ "organohaloaluminate," ^{195,196} and chloride-containing electrolytes. ⁵³ These early Mg electrolytes suffered from low anodic stability and corrosive effects when in contact with stainless steel cell components. ^{196,197} Recent efforts have honed in on weakly coordinating Mg²⁺ compounds containing boron. ^{198–202} As understanding of Mg SEI and electrolyte design advances, these new developments may be tested within the Mg-S system and perhaps eventually enable practical Mg-S batteries.

Much remains to be explored in the SIB space. The high degree of structural degradation observed in LiNaFeS2 when cycled in a Na cell is a common issue with layered transition metal chalcogenide sodium cathodes. The deleterious phase transitions suffered by layered sodium materials are attributed to Na⁺'s ability to stabilize multiple coordination geometries, whose favorability is electrostatically governed throughout cycling as depletion of the alkali layer reduces shielding between adjacent transition metal layers, or generally due to the larger diffusion pathways necessary for Na⁺ mobility.^{170,171} To offset these phase transitions or reduce material strain several strategies can be employed. Increasing the entropy of the material decreases the number of equivalent positions that are accessible between the pristine and discharged states,¹⁷⁰ and using pillar ions to increase shielding between the transition metal layers in highly dissociated states also discourages phase transitions. These pillar ions are either more charged than Na+ or larger to increase the electrostatic shielding effect and increase the size of diffusion channels.^{203,204} Amorphization of materials or otherwise purposeful introduction of defects may also lead to more dissipated strain experienced during cycling.¹³⁵

Another potential way to decrease structural degradation in Na batteries but specifically in anion redox cathodes is to enhance the delocalization of charge compensation, thus reducing the bond forming and breaking occurring during cycling that appears to be associated with high hysteresis. Examples of these kinds of systems include Na₂RuO₃¹⁰² and Na₂Mn₃O₇.^{108,111} In the last chapter, we studied Na-Cu-Fe-S materials that are highly covalent. Even in systems with distributed charge compensation, it appears as though fundamental limits in oxidation exist. Previous reports have cited Cu substitution, typically in the 2+ oxidation state, in smaller amounts in layered transition metal oxides as having a stabilizing effect. ^{205,206} However, Cu is typically present as a 1+ ion in sulfide materials. Research into whether smaller substitutions of Cu¹⁺ into sulfide materials can also increase phase stability during cycling could be useful. Additionally, the extent to which anion redox hysteresis can be reduced through engineering measures has not received much attention. Systematically testing the effects of different milling techniques along controlling cathode particle size and morphology may aid in decreasing the voltage hysteresis without more drastic changes in cathode composition and chemistry. In summary, the study of SIBs is an exciting field with high potential and much left to explore. As interest in SIBs continues to increase, we can expect further work in the field of SIB anion redox as well.

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SUPPLEMENTARY INFORMATION

5.1 Supplementary Figures for Chapter II

UV-Vis spectroscopy



Figure S1: UV-Vis spectra of S_8 , l-MgPS, and s-MgPS solutions from Figure 1 of the main text with the S_8 spectrum subtracted to display the relative differences in polysulfide speciation.



Figure S2: (a) Spectra for S_8 , l-MgPS, and s-MgPS at 0.4 mM S display evidence of polysulfide species in the MgPS solutions but not in the S_8 solution. Visible solids had crashed out of the s-MgPS solution at the time of dilution, so absorbance areas are not representative of the total amount of sulfur species in solution at the time of synthesis and electrochemical testing. (b) Spectra for S_8 diluted to 0.4 mM S and 0.2 mM S are shown. The peak positions do not change upon dilution, and absorbances <1.0 are well within the instrument detection limits and confirm different speciation in the solutions.



Figure S3: UV-Vis spectra of two synthesized 1-MgPS batches. 1-MgPS 1 and 1-MgPS 2 were diluted from synthesis concentrations by a factor of 10 with MACC-Mg(HMDS)₂ prior to obtaining spectra. 1-MgPS 2 was concentrated prior to dilution as detailed in the Experimental section. 1-MgPS 1 dil was diluted by a factor of 80 with MACC-Mg(HMDS)₂ prior to obtaining spectra, while 1-MgPS 2 dil was diluted by a factor of 10 with MACC-Mg(HMDS)₂ from the solution as synthesized. Both batches show the same polysulfide speciation.



Figure S4: UV-Vis spectra of two batches of 1-MgPS over cycling. All voltages are with respect to a Ag_2S quasi-reference electrode. (a) 1-MgPS 1 from solutions cycled to voltages of -2.65 V and -4.20 V vs. Ag_2S (after cycling for 9.5 and 56 hours, respectively). (b) 1-MgPS 2 from solutions cycled to voltages of -2.75 and -3.10 V vs. Ag_2S (after cycling for 29 and 56 hours, respectively). The differences in voltages and cycling times arise from the difference in voltages at which the experiments experienced voltage plateaus. 1-MgPS 2 init was concentrated prior to dilution as detailed in the Experimental section. Both batches show similar shifts in speciation and overall absorbance over the course of cycling.



Figure S5: UV-Vis spectra for each solution cycled to the passivation and electrolyte decomposition regimes: (a) neat electrolyte, (b) S_8 (62.4 mM S), (c) 1-MgPS (62.4 mM S), (d) s-MgPS (62.4 mM S), and (e) s-MgPS (39.9 mM S). All solutions are diluted by a factor of 10 with MACC–Mg(HMDS)₂ prior to analysis. All cells show a decrease in overall sulfur species-related absorbance over the course of cycling, although this is difficult to see with (d) s-MgPS that only cycled for 4.5 hours. In (d) s-MgPS at a lower concentration cycled for 45 hours, depletion of sulfur species-related absorbance is observed. (b) The S_8 only solution initially shows an increase in overall absorbance at potentials more negative than -2.4 V vs. Ag_2S attributed to previously suspended S_8 going into solution, and the appearance of long-chain polysulfides due to electrochemical cycling. (c) The 1-MgPS solution shows a relative retention of long-chain polysulfides over the course of cycling compared to a significant depletion in the dissolved S_8 region.



Figure S6: UV-Vis spectra of S_8 , l-MgPS, and s-MgPS solutions after cycling to voltages <-2.4 V (initial) and the same cycled solutions 15 minutes after 10 mg mL⁻¹ S_8 addition (after + S_8) with no further electrochemical cycling. The maximum absorbances in each spectrum have been normalized to one to allow for better comparison in speciation differences.

Chronopotentiometry

As-synthesized solutions



Figure S7: Expanded regions of interest from Figure 3 measured during the standard cycling experiment of Mg $|MACC-Mg(HMDS)_2|Mg$ cells with a Ag₂S quasireference electrode. Electrolyte additives are varied with (a) neat electrolyte and electrolyte with added S₈ and (b) added 1-MgPS and added s-MgPS. The results show that the rate of passivation is dependent on the polysulfide solution, with the solutions containing higher proportions of long-chain polysulfides passivating more slowly.



Figure S8: Expanded regions of interest of the potential transients from Figure 4 measured during the standard cycling experiment of $Mg|MACC-Mg(HMDS)_2|Mg$ cells with a Ag_2S quasi-reference electrode. The concentration is varied for (a) I-MgPS and (b) s-MgPS. The results show that passivation behavior is dependent on polysulfide concentration.



Figure S9: Transient potentials measured during the standard cycling experiment for Mg $|MACC-Mg(HMDS)_2|Mg$ cells relative to a Ag₂S quasi-reference electrode cells and no dissolved S₈. Duplicate data are shown to convey the typical variability.



Figure S10: Transient potentials measured during the standard cycling experiment for Mg $|MACC-Mg(HMDS)_2 + S_8|Mg$ cells relative to a Ag₂S quasi-reference electrode. Triplicate data are shown to convey the typical variability.



Figure S11: Transient potentials measured during the standard cycling experiment for Mg $|MACC-Mg(HMDS)_2 + 1-MgPS 1|Mg$ cells relative to a Ag₂S quasi-reference electrode. Triplicate data are shown to convey the typical variability.



Figure S12: Transient potentials measured during the standard cycling experiment for Mg $|MACC-Mg(HMDS)_2+1-MgPS 2|Mg$ cells relative to a Ag₂S quasi-reference electrode. Duplicate data are shown to convey the typical variability.



Figure S13: Transient potentials measured during the standard cycling experiment for Mg $|MACC-Mg(HMDS)_2 + s-MgPS|Mg$ cells relative to a Ag₂S quasi-reference electrode. Duplicate data are shown to convey the typical variability.
As-synthesized solutions with S_8 addition



Figure S14: Transient potentials measured during the standard cycling experiment for Mg $|MACC-Mg(HMDS)_2|Mg$ cells relative to a Ag₂S quasi-reference electrode and S₈ (312 mM S) added at the time indicated by the dashed red line. Triplicate data are shown to convey the typical variability.



Figure S15: Transient potentials measured during the standard cycling experiment for Mg $|MACC-Mg(HMDS)_2 + S_8|Mg$ cells relative to a Ag₂S reference electrode in with S₈ (312 mM S) added at the time indicated by the dashed red line. Triplicate data are shown to convey the typical variability.



Figure S16: Transient potentials measured during the standard cycling experiment for Mg|MACC-Mg(HMDS)₂+l-MgPS 1|Mg cells relative to a Ag₂S reference electrode with S₈ (312 mM S) added at the time indicated by the dashed red line. Triplicate data are shown to convey the typical variability.



Figure S17: Transient potentials measured during the standard cycling experiment for Mg $|MACC-Mg(HMDS)_2 + 1-MgPS 2|Mg$ cells relative to a Ag₂S reference electrode cells with S₈ (312 mM S) added at the time indicated by the dashed red line. Triplicate data are shown to convey the typical variability.



Figure S18: Transient potentials measured during the standard cycling experiment $Mg|MACC-Mg(HMDS)_2 + s-MgPS|Mg$ cells relative to a Ag_2S reference electrode with S_8 (312 mM S) added prior to cycling. Triplicate data are shown to convey the typical variability.

Electrode characterization MACC-Mg(HMDS)₂ electrolyte



Figure S19: EDS of (a) Mg, (b) Cl, and (c) O and (d) SEM on a Mg electrodein MACC–Mg(HMDS)₂ for 21 hours. 21 hours is the time it takes for the potential in a S_8 solution with a 62.4 mM concentration of S to reach -2.60 V vs. Ag_2S . The EDS shows the presence of chlorine and oxygen in regions associated with uneven morphologies seen in SEM.



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Figure S20: EDS of (a) Mg, (b) Cl, and (c) O and (d) SEM on a Mg electrode cycled in MACC-Mg(HMDS)₂ for 67 hours. 67 hours is the time it takes for the potential in a S_8 solution with a 62.4 mM concentration of S to reach -4.24 V vs. Ag₂S. EDS shows the presence of chlorine and oxygen in regions associated with uneven morphologies in the SEM. The SEM shows some more uneven deposition morphologies than an electrode cycled in the same solution to the time at which potentials of -2.60 V vs. Ag₂S are observed in a S_8 solution.





Figure S21: XPS of the Mg 2p and S 2p regions of Mg electrodes cycled in MACC–Mg(HMDS)₂ for (a-b) 21 hours and (c-d) 67 hours. 21 hours and 67 hours are the cycling times required for the potential in a S₈ solution with a 62.4 mM concentration of S to reach -2.60 V and -4.24 V, respectively. At the -2.60 V vs. Ag₂S equivalent time, the electrode shows (a) Mg 2p peaks at 47.6, 48.7, and 50.2 eV, with the first two binding energies assigned to manganese impurities in the overlapping Mn 3p region and MACC–Mg(HMDS)₂ decomposition products.^{69,70} The last binding energy is assigned to Mg/MgO species^{68,71,72,207}. The XPS shows (b) no peaks in the S 2p region. At the -4.24 V vs. Ag₂S equivalent time, the electrode shows (c) Mg 2p peaks at 50.0 and 51.5 eV assigned to Mg/MgO and MgCl₂, respectively,^{68,71,72,207} and (d) no peaks in the S 2p region.

S₈ in MACC-Mg(HMDS)₂ electrolyte



Figure S22: EDS of (a) Mg, (b) S, (c) Cl, and (d) O and (e) SEM on a Mg electrode cycled in S_8 to -2.60 V vs. Ag_2S . The EDS shows the presence of chlorine and oxygen in regions associated with uneven morphologies in the SEM. The SEM shows uneven deposition morphologies more uniformly present than in the electrode cycled for the equivalent time in MACC-Mg(HMDS)₂.



Figure S23: EDS of (a) Mg, (b) S, (c) Cl, and (d) O and (e) SEM on a Mg electrode cycled in S_8 solution to -4.24 V vs. Ag_2S . The EDS shows the presence of sulfur, chlorine, and oxygen. The SEM shows deposition morphologies more uneven than those present on the electrode cycled to -2.60 V vs. Ag_2S in S_8 solutions, and the deposits are insulating as indicated by prominent charging.





Figure S24: XPS of the Mg 2p and S 2p regions of Mg electrodes cycled to -2.60 V (a-b) and -4.24 V (c-d) vs. Ag_2S in S_8 solution. The electrode cycled to -2.60 V vs. Ag_2S shows peaks in (a) the Mg 2p region at 50.0 eV assigned to Mg/MgO/MgS_x species, 68,71,72,207 and (b) S $2p_{3/2}$ at 162.9 and 168.3 eV which are attributed to MgS_x and trace MgSO₃ species, respectively. $^{52,73-75,208}$ For the electrode cycled to -4.24 V vs. Ag_2S , there are peaks in (a) the Mg 2p region at 50.3 eV assigned to Mg/MgO/MgSx species, 68,71,72,207 and (b) the S $2p_{3/2}$ peaks at 163.6 and 168.4 eV are assigned to MgS_x and trace MgSO₃ species, respectively. $^{52,73-75,208}$

l-MgPS in MACC-Mg(HMDS)₂ electrolyte



Figure S25: HRSEM image of a Mg electrode cycled in l-MgPS to -2.65 V vs. Ag_2S . The HRSEM shows darker and lighter areas on the sample, suggesting uneven deposition morphology.



Figure S26: EDS map sum spectra for a Mg electrode cycled in neat electrolyte $MACC-Mg(HMDS)_2$ to (a) -1.75 V and (b) -1.65 V vs. Ag_2S , as well as a Mg electrode cycled in 1-MgPS to (c) -2.65 V and (d) -4.20 V vs. Ag_2S . All spectra show O, Mg, trace Al, and Cl. Electrodes cycled to both voltages in 1-MgPS show traces of S, with a larger proportion of S visible in the spectrum for the electrode cycled to -4.20 V vs. Ag_2S .



Figure S27: XPS of the Mg 2p (a, e), S 2p (b, f), Cl 2p (c, g), and C 1s (d, h) regions of Mg electrodes cycled in l-MgPS to -2.65 V vs. Ag_2S (a-d) and -4.20 V vs. Ag_2S (e-h).

s-MgPS in MACC-Mg(HMDS)₂ electrolyte



Figure S28: EDS of (a) Mg, (b) S, (c) Cl, and (d) O and (e) SEM on a Mg electrode cycled in s-MgPS to -2.75 V vs. Ag_2S . The EDS shows the presence of sulfur, chlorine, and oxygen. The SEM shows uneven deposition morphologies similar to those present in the electrode cycled to similar voltages in S₈ solution with a 62.4 mM concentration of S.



Figure S29: EDS of (a) Mg, (b) S, (c) Cl, and (d) O and (e) SEM on a Mg electrode cycled in s-MgPS to -5.80 V vs. Ag_2S . The EDS shows the presence of sulfur, chlorine, and oxygen. The SEM shows uneven deposition morphologies more uniformly present than in the electrode cycled to -2.75 V vs. Ag_2S in s-MgPS, and the deposits are insulating as indicated by prominent charging.

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Figure S30: XPS of the Mg 2p and S 2p regions of Mg electrodes cycled to - 2.75 V (a-b) and -5.80 V (c-d) vs. Ag_2S in s-MgPS solution. For the electrode cycled to -2.75 V vs. Ag_2S , there are peaks in (a) the Mg 2p region at 50.1 eV attributed to Mg/MgO/MgS_x species,^{68,71,72,207} and (b) the S $2p_{3/2}$ peak at 163.2 eV is attributed to MgS_x.^{52,73–75} The electrode cycled to -5.80 V vs. Ag_2S shows peaks in (c) the Mg 2p region at 49.3 and 49.7 eV. The 49.3 eV peak is assigned to Mg/MACC–Mg(HMDS)₂ decomposition species, 49.7 eV corresponds to Mg/MgO/MgS_x species.^{52,73–75} (d) The S $2p_{3/2}$ peak at 161.7 eV is assigned to MgS_x species.^{52,73–75}

Characterization for XPS assignments



Figure S31: XPS of the Mg 2p and S 2p regions of an MgS standard. (a) Mg 2p peak at 50.0 eV and (b) S $2p_{3/2}$ peak at 160.6 eV.

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in wt.% (1 Sigma)
Magnesium	12	K-series	11863236	106.8444036	99.89600587	99.9532757	0
Calcium	20	K-series	51666	0.020161154	0.018850016	0.011438003	0
Vanadium	23	K-series	132870	0.017901261	0.01673709	0.00799011	0
Manganese	25	K-series	394091	0.028043707	0.026219945	0.011606558	0
Zinc	30	K-series	1534441	0.045121452	0.042187075	0.015689627	0
Rhodium	45	K-series	1514370	0	0	0	0
Oxygen	8		0	0	0	0	0
			Sum:	106.9556312	100	100	

Figure S32: Table showing XRF analysis of scraped Mg foil. Notable impurities include manganese, zinc, and calcium.

5.2 Supplementary Figures for Chapter III Spectroscopic Characterization for SI

Samples for ex-situ X-ray absorption spectrosopy (XAS) were prepared in 2032 coin cells as previously described for electrochemical experiments. The cells were cycled to the second charge to 2.5 V and disassembled. After disassembly any visibly remaining GFD was manually scraped off the cathode surface, and the cathodes were subsequently washed with DMC and dried under vacuum at 60° C for 6 h. The dried cathodes were then crushed into fine powders. Fe K-edge and S K-edge XAS were measured at beamline 4-3 at the Stanford Synchrotron Radiation Lightsource at SLAC National Accelerator Laboratory. For analysis, the dried powders were directly loaded into stainless steel holders provided by beamline 4-3 with Kapton tape on either side for Fe K-edge XAS, or diluted to ~5 wt% S concentrations with boron nitride prior to being adhered to a stainless steel holder with tape and polypropylene for S K-edge XAS. All sample preparation was conducted inside an Ar-filled glovebox. Fe K-edge data were calibrated to a collinear Fe foil present for each sample. Fe K-edge XAS measurements were conducted in transmission mode while S K-edge XAS measurements were conducted in fluorescence mode. For each spectrum 2 scans were averaged.



Figure S33: Synchrotron XRD patterns for LiNaFeS₂ synthesized at (a) 500°C with quenching and (b) 600°C without quenching. Positions of LiNaFeS₂ reflections, the fit from Rietveldt refinement, and difference between the data and fit are also depicted.



Figure S34: Long-term (a) charge and (b) discharge capacities for $LiNaFeS_2$ cycled in Li and Na half cells at C/10.



Figure S35: Fe K-edge of LiNaFeS₂ in the (a) pristine state and charged to the ~2.5 V plateau during the (b) first charge and (c) second charge in Li and Na half-cells. S K-edge of LiNaFeS₂ in the (d) pristine state and charged to the ~2.5 V plateau during the (e) first charge and (f) second charge in Li and Na half-cells. Data in panels (c) and (f) were collected as described in the SI section from beamline 4-3 at SSRL.



Figure S36: *Ex-situ* SEM pictures of LiNaFeS₂ cathodes in the (a) pristine state and discharged at C/10 in a (b) Li half cell to 1.7 V vs. Li and in a (c) Na half cell to 1.1 V vs. Na.



Figure S37: *Ex-situ* SEM pictures with Fe EDS overlays of $LiNaFeS_2$ cathodes in the (a) pristine state and discharged at C/10 in a (b) Li half cell to 1.7 V vs. Li and in a (c) Na half cell to 1.1 V vs. Na.



Figure S38: *Ex-situ* SEM pictures with S EDS overlays of $LiNaFeS_2$ cathodes in the (a) pristine state and discharged at C/10 in a (b) Li half cell to 1.7 V vs. Li and in a (c) Na half cell to 1.1 V vs. Na.

[This section is temporarily embargoed]