

Investigation of Alkali Metal-Host Interactions and Electrode-Electrolyte  
Interfacial Chemistries for “Lean” Lithium and Sodium Metal Batteries

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# Investigation of Alkali Metal-Host Interactions and Electrode-Electrolyte Interfacial Chemistries for “Lean” Lithium and Sodium Metal Batteries

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## ABSTRACT

The development and commercialization of alkali ion secondary batteries has played a critical role in the development of personal electronics and electric vehicles. The recent increase in demand for electric vehicles has pushed for lighter batteries with a higher energy density to reduce the weight of the vehicle while with an emphasis on improving the mile range. A resurgence has occurred in lithium, and sodium, metal anode research due to their high theoretical capacities, low densities, and low redox potentials. However, Li and Na metal anodes suffer from major safety issues and long-term cycling stability. This dissertation focuses on the investigation of the interfacial chemistries between alkali metal-carbon host interactions and the electrode-electrolyte interactions of the cathode and anode with boron-based electrolytes to establish design rules for “lean” alkali metal composite anodes and improve long-term stability to enable alkali metal batteries for practical electrochemical applications.

Chapter 2 of this thesis focuses on the design and preliminary investigation of “lean” lithium-carbon nanofiber ( $<5 \text{ mAh cm}^{-2}$ ) composite anodes in full cell testing using a  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC 622) cathode. We used the electrodeposition method to synthesize the Li-CNF composite anodes with a range of electrodeposition capacities and current densities and electrolyte formulations. Increasing the electrodeposition capacity improved the cycle life with  $3 \text{ mAh cm}^{-2}$  areal capacity and 2% vinylene carbonate (VC) electrolyte additive gave the best cycle life before reaching a state of “rapid cell failure”. Increasing the electrodeposition rate reduced cycling stability and had a faster fade in capacity. The electrodeposition of lithium metal into a 2D

graphite anode significantly improved cycle life, implying the increased crystallinity of the carbon substrate promotes improved anode stability and cycling capabilities.

As the increased crystallinity of the carbon anode was shown to improve the “lean” composite anode’s performance, Chapter 3 focuses on utilizing a CNF electrode designed with a higher degree of graphitization and probing the interacting mechanism of Li and Na with the CNF host. Characterization of the CNF properties found the material to be more reminiscent of hard carbon materials. Electrochemical analysis showed better long-term performance for Na-CNF symmetric cells. Kinetic analysis, using cyclic voltammetry (CV), revealed that Na ions successfully (de)intercalated within the CNF crystalline interlayers, while Li ions were limited to surface adsorption. A change in mechanism was quickly observed in the Na-CNF symmetric cycling from metal stripping/plating to ion intercalation/deintercalation, enabling the superior cycling stability of the composite anode. Improving the Na metal stability is necessary for enabling Na-CNF improved long-term performance.

Sodium batteries have begun to garner more attention for grid storage applications due to their overall lower cost and less volumetric constraint required. However, sodium cathodes have poor electrode-electrolyte stability, leading to nanocracks in the cathode particles and transition metal dissolution. Chapter 4 focuses on electrolyte engineering with the boron salts sodium difluoro(oxolato)borate (NaDFOB) and sodium tetrafluoroborate ( $\text{NaBF}_4$ ) mixed together with sodium hexafluorophosphate ( $\text{NaPF}_6$ ) to improve the electrode-electrolyte compatibility and cathode particle stability. The electrolytes containing NaDFOB showed improved electrochemical stability at various temperatures, the formation of a more robust electrode-electrolyte interphase, and suppression in transition metal (TM) reduction and dissolution of the cathode particles measured after cycling.

In Chapter 5, we focus on the electrochemical properties and the anode-electrolyte interfacial chemistry properties of the sodium borate salt electrolytes. Similar to Chapter 4, the NaDFOB containing electrolytes have improved electrochemical performance and stability. Following the same electrodeposition parameters as Chapter 2, we find the NaDFOB electrolytes improves the stability of electrodeposited Na metal and the “lean” composite anode’s cyclability. This study suggests the great potential for the NaDFOB electrolytes for Na ion battery applications.

Investigation of Alkali Metal-Host and Electrode-Electrolyte Interfacial Chemistries for  
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GENERAL AUDIENCE ABSTRACT

The ever-increasing demand for high energy storage in personal electronics, electric vehicles, and grid energy storage has driven for research to safely enable alkali metal (Li and Na) anodes for practical energy storage applications. Key research efforts have focused on developing alkali metal composite anodes, as well as improving the electrode-electrolyte interfacial chemistries. A fundamental understanding of the electrode interactions with the electrolyte or host materials is necessary to progress towards safer batteries and better battery material design for long-term applications. Improving the interfacial interactions between the host-guest or electrode-electrolyte interfaces allows for more efficient charge transfer processes to occur, reduces interfacial resistance, and improves overall stability within the battery. As a result, there is great potential in understanding the host-guest and electrode-electrolyte interactions for the design of longer-lasting and safer batteries.

This dissertation focuses on probing the interfacial chemistries of the battery materials to enable “lean” alkali metal composite anodes and improve electrode stability through electrolyte interactions. The anode-host interactions are first explored through preliminary design development for “lean” alkali composite anodes using carbon nanofiber (CNF) electrodes. The effect on increasing the crystallinity of the CNF host on the Li- and Na-CNF interactions for enhanced electrochemical performance and stability is then investigated. In an effort to improve the capabilities of Na batteries, the electrode-electrolyte interactions of the cathode- and anode-electrolyte interfacial chemistries using sodium borate salts are probed using electrochemical and

X-ray analysis. Overall, this dissertation explores how the interfacial interactions affect, and improve, battery performance and stability. This work provides insights for understanding alkali metal-host and electrode-electrolyte properties and guidance for potential future research of the stabilization for Li- and Na-metal batteries.

## Acknowledgements

First, I would like to thank and acknowledge my advisor Dr. Feng Lin. Without his guidance and support, none of the research and discussion presented throughout this dissertation would be possible. Being a part of Dr. Lin's first batch and helping build the lab with him over these five years has been an incredible experience that has improved my understanding and admiration of the operations of lab development. He has always been available for support and discussion in my academic and personal life and has helped lift me up from slumps and roadblocks I have undergone throughout my time under his tutelage. His guidance has helped prepare me for a successful future as an independent scientist. I am grateful for joining the Lin lab and for the friends and connections I have made along the way.

My thanks to my committee members, Professors Robert Moore, Guoliang (Greg) Liu, and Louis Madsen for the assistance throughout my academic career. The comments from my literature review, committee meetings, and internal seminar has helped guide me to better understanding of the fundamental chemistry behind my experiments. I am appreciative of the "tough love" I have received from my committee; teaching me to look deeper into the fundamental science.

I want to thank all my lab mates that I have gotten to know and develop friendships with over my time at Virginia Tech. The academic, and personal, discussions I have had over the years are invaluable and I am appreciative to have gotten to know a great group of people, and scientists. I would like to extend an acknowledgement and thanks to our first postdoc Dr. Linqin Mu who has started the lab with us and has always been ready, and willing, for discussions on data analysis, measurements, experiments, and general chatting and has been a great friend over the years. I would like to thank those that started the journey with me in the beginning phases of the Lin lab,

specifically Linqin Mu, Muhammad Mominur Rahman, Crystal Waters, and James Steiner and all the unique experiences that came along with setting up a new lab and starting with a new PI. I also extend me thanks to Zhengrui Xu, Stephanie Spence, Lei Tao, Zhijie Yang, Yuxin Zhang, Dong Hou, Chunguang Kuai, Huabin Sun, and Mingyu Yuan for your support and friendship. I also extend thanks to the beamline scientists Dennis Nordlund at SLAC national accelerator laboratory and Luxi Li and Cheng-Jun Sun at Argonne national laboratory for their assistance in performing synchrotron experiments and processing data.

I would like to thank my soon-to-be wife Mary Rose Canlas who has been with me and supported me for over 8 years. From our time meeting each other during the University of Guam Biology Club haunted house, to hanging out and studying in the science building after-hours, to moving to Virginia and spending these five years together and building our “family” of now three dogs and three cats. I am appreciative for all the support and encouragement you have given me throughout graduate school. You have helped me get to where I am today, and I am lucky for you being in my life. I am also grateful for having your amazing family that is always there supporting us, checking in on us, and constantly sending goodies and reminders of back home.

Lastly, my parents David Kautz Sr. and Kelly Marsh who have always given me endless support throughout my life, and especially throughout my academic career. You have always given me unconditional love throughout my life and have supported whatever path I have chosen. I am eternally grateful for your guidance, helping shape me into the person I am today. I wish we did not have to live eight thousand miles apart, but knowing you are always there for me eases the longing of having you nearby.

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## Attributions

In this dissertation, Chapter 2 is a reprint of a manuscript published in the Journal of Materials Chemistry A. David Kautz prepared and characterized the Li-CNF composite anodes and performed materials characterization and all electrochemical experiments. Lei Tao and Zhifeng Zheng synthesized the CNF. Linqin Mu synthesized the cathode precursor materials. Xu Feng performed lab XPS and assisted with data analysis. Dennis Nordlund performed preliminary synchrotron XPS experiments. Dr. Feng Lin, principal investigator (PI), supervised the research project, provided technical insight during experimentation, and assisted in writing and editing. All coauthors participated in the discussion of the project and manuscript.

Chapter 3 is an unpublished manuscript under preparation for submission. David Kautz prepared the Li- and Na-CNF composite anodes, performed SEM imaging, XPS and Raman data analysis and all electrochemical measurements. Lei Tao and Zhifeng Zheng synthesized the CNF. Linqin Mu synthesized the cathode precursor materials. Muhammad Mominur Rahman conducted the XRD measurements. Chunguang Kuai performed TEM imaging. Lei Tao and Linqin Mu participated in the data discussion. Dr. Feng Lin, principal investigator (PI), supervised the research project, provided technical insight during experimentation, and assisted in writing and editing. All coauthors participated in the discussion of the project and manuscript.

Chapter 4 is an unpublished manuscript under preparation for submission. David Kautz synthesized and characterized the cathode materials and electrolyte compositions and performed all electrochemical measurements. Linqin Mu assisted in synthesizing cathode precursor materials. Lina Gao and Xueqian Kong synthesized the NaDFOB salt. Muhammad Mominur Rahman conducted the XRD measurements and Dong Hou assisted in converting synchrotron XRD data.

Luxi Li performed XFM measurements. Sami Sainio and Dennis Nordlund performed soft XAS measurements. Chengjun Sun performed the hard XAS measurements. Dr. Feng Lin, principal investigator (PI), supervised the research project, provided technical insight during experimentation, and assisted in writing and editing. All coauthors participated in the discussion of the project and manuscript.

Chapter 5 is an unpublished manuscript under preparation for submission. David Kautz synthesized and characterized the electrolyte compositions and performed all electrochemical measurements and XPS data analysis. Dr. Feng Lin, principal investigator (PI), supervised the research project, provided technical insight during experimentation, and assisted in writing and editing.

# 1. Introduction

## 1.1 Research Motivation

Batteries have become a prevalent aspect of modern society; they are an important part of the everyday life of the average person. Powering cellphones, laptops, and much more, batteries are important in keeping important necessary technologies functioning. With the ever-increasing energy demands of current and advancing technologies a longer lasting and more powerful battery is necessary. Commercial Lithium ion (Li-ion) intercalating anodes (i.e., graphite) are hypothesized to have their practical capacity reach their theoretical capacity ( $372 \text{ mAh g}^{-1}$ ) in the near future. Li metal is seen as the best choice for the future of anode materials, often being dubbed the “Holy Grail” of anode materials, having the highest theoretical capacity ( $3860 \text{ mAh g}^{-1}$ ), lowest electronegative potential ( $-3.040 \text{ V}$  vs Standard Hydrogen Electrode), and low density ( $0.534 \text{ g cm}^{-3}$ ). Li metal has great versatility being used in Li-S, Li-air, and standard Li metal batteries for next generation energy requirements.<sup>1-4</sup> Another promising material in recent research efforts is Na metal as an anode for grid energy storage and other large scale applications.<sup>5-7</sup> Sodium metal has a high theoretical capacity ( $1166 \text{ mAh g}^{-1}$ ), low electrochemical potential ( $-2.71 \text{ V}$  vs SHE), and reasonably low density ( $0.97 \text{ g cm}^{-3}$ ). Two of the main challenges preventing Li and Na metal batteries from commercialization are the formation of dendrites, high reactivity, and low Coulombic efficiency (CE).

Dendritic formation can cause potential short circuit of the battery which can lead to some safety hazards and low cycle life. In Figure 1.1, the main challenges of alkali metal anodes are shown. The high reactivity and infinite relative volume change of metallic lithium or sodium leads to excessive electrolyte decomposition, and dendrite growth formation.<sup>8</sup> The dendritic growth has

two main mechanisms, to grow until there is a short circuit, or physically detach from the metal anode, and becoming a “dead material”; increasing the loss of active Li or Na and consumption of electrolyte. This also leads to high surface area and lower CE performance of the anode. Low CE can be alleviated by having an excess of Li or Na present and by modifying the electrolyte system. My project involves utilizing carbonaceous host materials to house lithium and sodium within the carbonaceous matrix, in order to utilize a “lean” loading ( $<5 \text{ mAh cm}^{-2}$ ) of Li and Na metal and improve cell life.

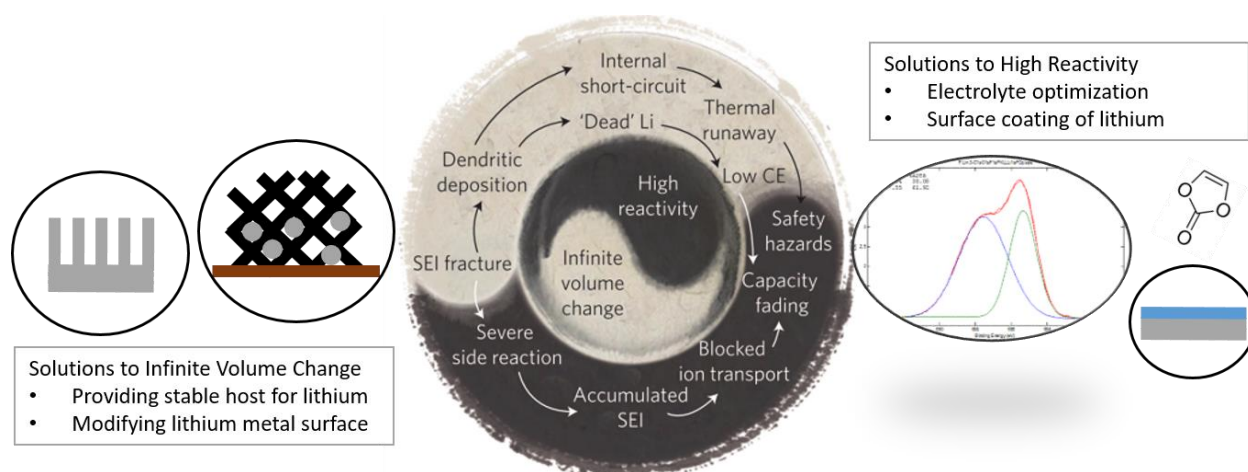


**Figure 1.1** The main challenges of alkali metal anodes originating from the relative infinite volume expansion of lithium metal (silver) and its high reactivity (black) with solutions that will help address the challenges of lithium metal anodes. Adapted from ref. 8 with permission. Copyright 2017, Springer Nature.

Metallic Li anode research began in the 1970’s by Stanley Whittingham at Exxon<sup>8</sup>, and was shortly commercialized by Moli Energy in the late 1980’s, but was soon discontinued due to safety issues. The emergence of Li-ion batteries in 1991 by Sony, shifted the focus from Li metal to the more manageable graphite anodes, not being plagued by the problems present in Li metal.<sup>9</sup> As Li-ion batteries are reaching their theoretical capacity, Li metal anode research has reemerged in the early 2000’s and has improved our understanding of the mechanisms and challenges of the

chemistry present in Li metal anodes. With this resurgence of research and deeper understanding of Li metal chemistry, the goal is to develop safer, more stable, and better performing Li anodes. There have been multiple studies modeling<sup>10,11</sup> and analyzing<sup>12–14</sup> dendritic growth behaviors. Among many approaches, a major approach to preventing dendrite formation has been through modifying the liquid electrolyte system and the interactions that lead to the formation of the solid electrolyte interphase (SEI) from the initial reaction between polarized alkali metal and the organic solvent in the electrolyte. This review will focus on the progress of lithium, sodium, and carbonaceous anode complexes as well as the electrolyte systems that have been thoroughly investigated and will discuss the direction that the future of lithium and sodium metal anodes may proceed in.

## **1.2. Anodes**

### **1.2.1 Carbon anodes**

Carbonaceous materials have been heavily researched as anode materials for Li ion secondary batteries over the past 50 years.<sup>15</sup> Graphite had won as the candidate anode of choice in 1991 when it was implemented in the first commercialized Li ion intercalation battery by Sony and has remained as the anode of choice over the past 30 years. Graphite is highly attractive due to its high practical specific capacity achieved ( $\sim 360 \text{ mAh g}^{-1}$ ), low operational voltage ( $\sim 0.1 \text{ V}$  vs.  $\text{Li}^+/\text{Li}$ ), stable long-term performance, and more.<sup>15–17</sup> Graphite consists of highly ordered graphene layers stacked parallel to each other and is held together from a combination of covalent bonding, metallic-like bonds, and weak van der Waals interactions. The intercalation of alkali metal ions into the interlayers of carbon materials leads to the formation of graphite intercalation compounds (GICs). The mixed ionic and electronic conducting properties of graphite contributes

to its ability to have electrochemical charge transfer mixed with intercalating guest ions through host-guest solid-state reactions. The  $\pi$ -bonds of the graphite interlayers overlaps with the p-orbitals of the guest alkali metal ions. This mechanism causes band effects and leads to a charge transfer mechanism between the alkali metal ions and the graphene layers (Figure 1.2).<sup>18,19</sup> However, while Li ions can easily intercalate into the graphite layers, the intercalation of Na ions is very limited.<sup>20–22</sup> The energy requirement for Na insertion into the smaller layer d-spacing of graphite (3.35 Å) is much higher than it is for lithium due to its larger size and weak chemical affinity to carbon (Figure 1.3b).<sup>22,23</sup> The d-spacing required for Na ions to intercalate equivalently to Li ions is  $\sim 3.7$ – $3.8$  Å (Figure 1.3c).<sup>23</sup> However, the chemical binding between the alkali metal ions and the GICs can significantly reduce when the d-spacing of the interlayers becomes too large.<sup>15,23</sup>

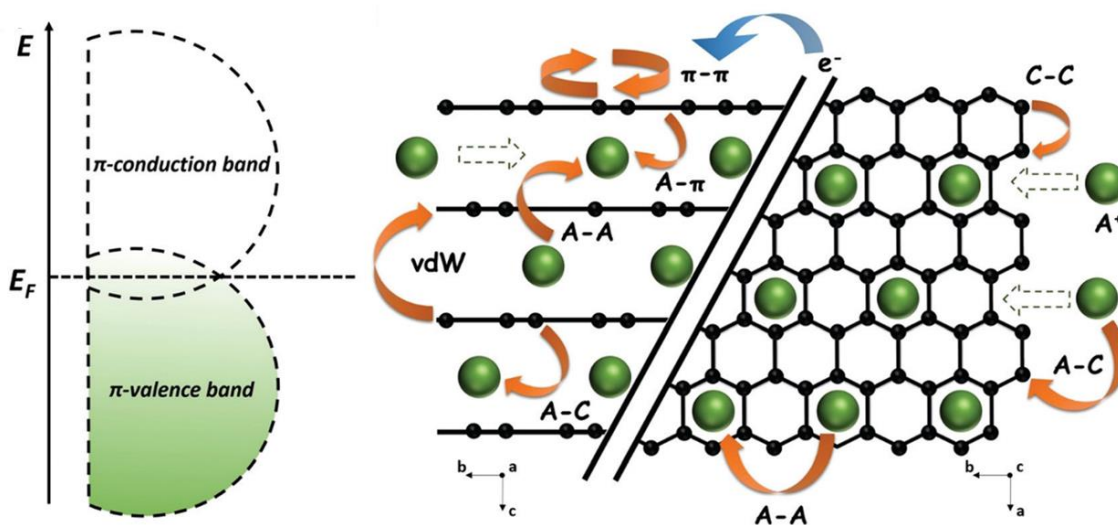


**Figure 1.2** Schematic of graphite band structure and alkali metal ion guest-host bonding interactions with graphite. Reproduced from ref. 15 with permission. Copyright 2019, Royal Society of Chemistry.

A relatively newer classification of carbon materials known as hard carbons has been shown to be a promising material for Na ion battery applications over the past decade. Hard carbons are generally classified semi-crystalline materials with highly defective structures.<sup>24,25</sup> The

interlayer d-spacing typically ranges from 3.6-3.9 Å and has a theoretical capacity of 279 mAh g<sup>-1</sup> (NaC<sub>8</sub> configuration) for Na ion batteries.<sup>24-27</sup> There is no uniform definition of hard carbons due the wide variety of precursors and bio-mass derivatives used to develop a wide assortment of unique structures.<sup>25-31</sup> The intercalation mechanism of Na ions into hard carbon is also heavily debated and still not entirely understood due the non-uniform nature of hard carbons. Overall, carbonaceous anodes have been the anode material of choice for commercialization due to their moderately high practical capacities, good cycling stability, and vast abundance. The intercalation chemistry of the guest-host interactions is heavily dependent on the crystallinity, interlayer spacing, and structure of the carbonaceous GIC host material.

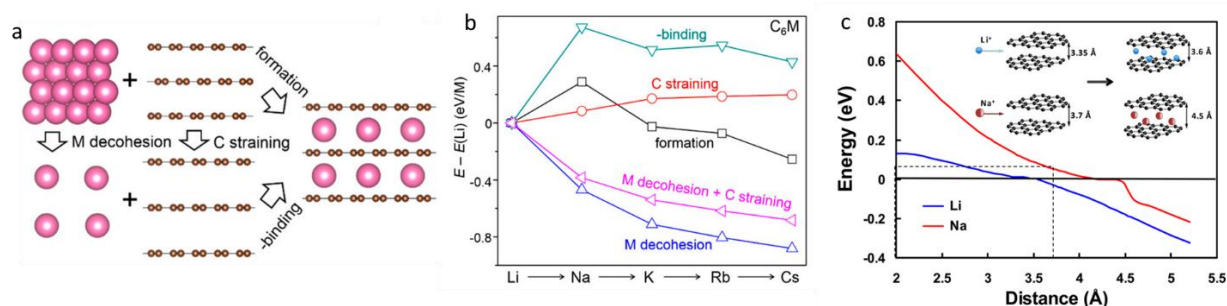


**Figure 1.3** a) Partition of the formation process of alkali metal-graphite compounds. b) The energetics of each step, relative to Li ion. Adapted from ref. 22 with permission. Copyright 2016, National Academy of Sciences. c) Theoretical energy cost of Li (blue) and Na (red) ion intercalation into ordered carbon interlayers as a function of interlayer d-spacing. Reproduced from ref. 23 with permission. Copyright 2012. American Chemical Society.

## 1.2.2 Li metal anode

In the past decade Li metal anode research has had a resurgence due to the current practical capacity of graphite anodes foretold to reach their theoretical limits in the near future. There is now a better understanding of the reactions and mechanisms of metallic lithium with various electrolyte systems and additives. Attempts to solve the challenges of using lithium metal anodes

for secondary batteries has diversified research into multiple paths, including but not limited to “next generation” lithium sulfur (Li-S), and lithium air (Li-O<sub>2</sub>) batteries.<sup>32–34</sup>

A thorough investigation of dendrite growth and propagation has shown that there are different mechanisms of dendrite growth correlating to different applied current densities. Dendrite growth mechanisms can interchange during further cycle life from “mossy-like” dendrite growth to the more damaging “fractal-like” growth pattern (Figure 1.4) that has the ability to pierce through separators that can lead to short-circuit failure.<sup>35</sup> Using Sand’s time equation, (eqn. 1)<sup>36</sup>, combined with optical microscopy, the change in lithium dendrite growth mechanisms, from mossy to dendritic growth, was found to be related to when the system becomes diffusion limited for Li ion migration on the surface of the lithium metal anode.<sup>36</sup> Recent developments have offered a promising future for lithium metal anodes to minimize dendritic growth and improve the anode’s stability via modifications to the topography of the surface of the lithium metal. The creation of a micro surface pattern morphology into the lithium metal anode has been shown to increase the CE, rate capability, and dendrite suppression, and have low impedance performance. This is attributed to increasing the surface area of the lithium anode and directing an increase of current density into the wells of the patterned lithium.<sup>37,38</sup>

Modeling studies of dendritic growth and behavior have been performed to better understand the propagation mechanism of lithium dendrites and how to avoid, or better prevent, one of the main barriers barring lithium metal anodes from being used in commercial applications.<sup>10,11</sup> Using in-situ optical microscopy, the behavior and characteristics of dendritic growth can be studied in real time.<sup>39,40</sup> “Hot spots”, in terms of increased charge density, form from pits in the lithium anode during inhomogeneous plating/stripping cycles, but the mechanism

is not well understood. There are critical criteria that require a resolution for further understanding of the mechanisms that cause lithium dendritic growth and excessive side reactions.<sup>39</sup>

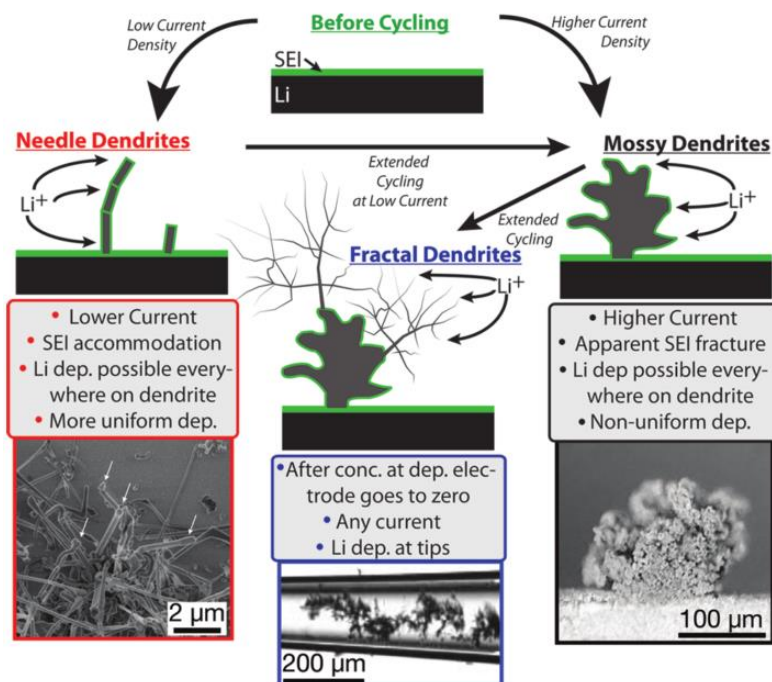


**Figure 1.4** Development of dendritic growth morphology depending on the applied current density and cycle life of the lithium metal anode. Reproduced from ref. 35 with permission. Copyright 2017, American Chemical Society.

$$t_{sand} = \pi D_{app} \frac{(z_c c_0 F)^2}{4(J t_a)^2} \quad (1)$$

### 1.2.3 Li-C composite anode

Recently, using carbonaceous material scaffolds designed to form a composite with Li metal has become a popular area of focus. The two main methods for Li insertion are via melt infusion and electrodeposition. Melt infusion allows lithium to fill in the entirety of the carbonaceous host network, becoming similar to Li metal visually. This method requires a “lithiophilic” substrate to allow for Li insertion to fill the carbon fiber host matrix (Figure 1.5a).

One of the first presentations of this method was by Zheng et al. showing the improved performance and stability and no observation of dendritic growth, which was attributed to having the CNF host network 3D matrix.<sup>41</sup> The 3D matrix allows for stable striping and plating of the Li metal, reducing loss of Li, capacity fading, and hysteresis compared to pure Li metal anode. Following this method, Lin et al. used a layered reduced graphene oxide (rGO) via sparking method for Li melt infusion to increase the films lithiophilicity and the inherent capillary force produced by the nanogaps.<sup>42</sup> The layered rGO structure allows for Li to fill in homogenously throughout the matrix and form a stable Li-C composite (Figure 1.5b). The lightweight and porous nature of the rGO contributes to the high capacity retention, low hysteresis, and improved cycling stability for this new class of Li-C anodes.<sup>42</sup> Both Li-C composite anodes via the melt infusion method result in large increases for practical specific capacity, compared to Li ion graphite anodes, being observed at 2,061 mAh/g and 3,390 mAh/g and account for 40% and 7% of the lithiated electrode's mass, respectively.<sup>13,14</sup> The volume expansion of both composite anodes are between 15-20% during charge and discharge cycles and are comparable to commercialized graphite anodes having 10% volume fluctuation.<sup>13,14</sup>

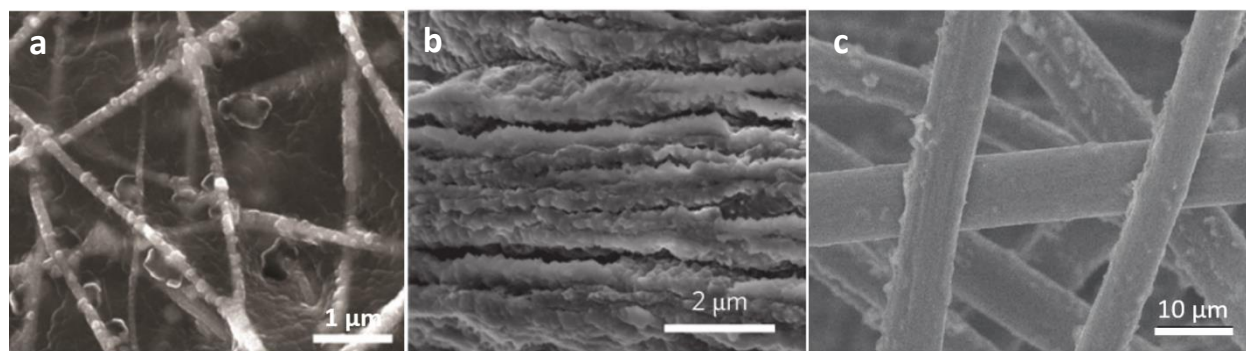


**Figure 1.5** SEM images of different methods for forming Li-C composite anodes for a) melt-infusion of a CNF matrix Reproduced from ref. 41 with permission. Copyright 2016, National Academy of Sciences. b) Melt-infusion of a layered reduced graphene oxide Reproduced from ref. 42 with permission. Copyright 2016, Springer Nature. c) Electrodeposition of lithium within a carbon fiber matrix. Reproduced from ref. 43 with permission. Copyright 2017, American Chemical Society. The lithium insertion method and type of carbon host material shows the difference in how lithium is stored in the carbon matrices.

Using the electrodeposition method, the amount of Li deposited can be controlled and studied, unlike with melt-infusion. Electrodeposition has two main stages: a nucleation phase and a growth phase. During the electrodeposition, as the voltage drops to 0 V, the lithium seeds begin to nucleate and form metallic lithium. Once below 0 V the growth phase begins, coating the carbon material with lithium forming a core shell structure (Figure 1.5c).<sup>43,44</sup> The composite anode shows increased CE and stability, compared to a Li metal disc. Depositing 8 mAh cm<sup>-2</sup> into the carbon fiber, the anode can retain 80% capacity at 0.5C rate after 300 cycles using a LiFePO<sub>4</sub> cathode with a cycling range of 2.0 – 4.0 V. There is a synergistic effect between the graphitic carbon and the metallic lithium by increasing electronic conductivity and  $\pi$  band and p-orbital interactions of the graphitic crystalline structure and Li ions, allowing for better Li ion transportation and capacity retention.<sup>[16]</sup>

#### **1.2.4 Na-C Composite Anode**

Following the trend of lithium metal research, the interest into sodium metal – carbon composite anode design has also increased within the past few years. However, due to the different interactions between Li and Na ions with carbon the design of carbon materials for Na-C composite anodes may require alternative approaches than what works for Li-C composite anodes. Modifying the graphitization content and size of the crystalline layers of hard carbon materials has been investigated to reduce the energy strain to intercalate into the carbon crystalline lattice and improve the interactions between Na ions and the carbon material.<sup>25–27,45</sup> Alternative methods to enhance the affinity for Na to bond to the carbon host material are modifying the surface functionalization of the carbonaceous substrate or doping the substrate with metals or metal oxide species. These surface modification methods can improve charge homogenization along the surface of the substrate and increase the sodiophilicity of the substrate through lowering the bonding energy

necessary for electrodeposition nucleation or sodium melt infusion.<sup>46,47</sup> Introducing more sodiophilic sites onto the substrate has also been shown to improve homogeneous stripping/plating of Na metal during cycling and improve the lifespan of the composite anode.<sup>46–50</sup>

Tao et al. used a lignin-derived CNF substrate with porous defects to improve the sodiophilicity of the substrate and facilitate the defect sites for sodium melt infusion.<sup>47</sup> Their anode was able to deliver a practical capacity of 1049 mAh g<sup>-1</sup>, 90% of the theoretical capacity of sodium metal. The Na-LCNF composite anode was able to achieve up to 790 hours of galvanostatic stripping/plating cycles before shorting, while a thick Na metal foil shorted after 350 hours and maintained smoother stripping/plating morphology while cycling (Figure 1.6a). In a full cell configuration, the composite anode maintained a better capacity retention and lower impedance in a full cell. Zheng et al. used hetero-atom doping of their CFs to improve the Na binding affinity and localized charge heterogeneity of their carbon substrate.<sup>50</sup> The hetero-atom doping reduced the nucleation overpotential required for Na metal electrodeposition (Figure 1.6b,c) and improved symmetric cycling stability when compared to Na metal and a Na-Cu foil composite anode.

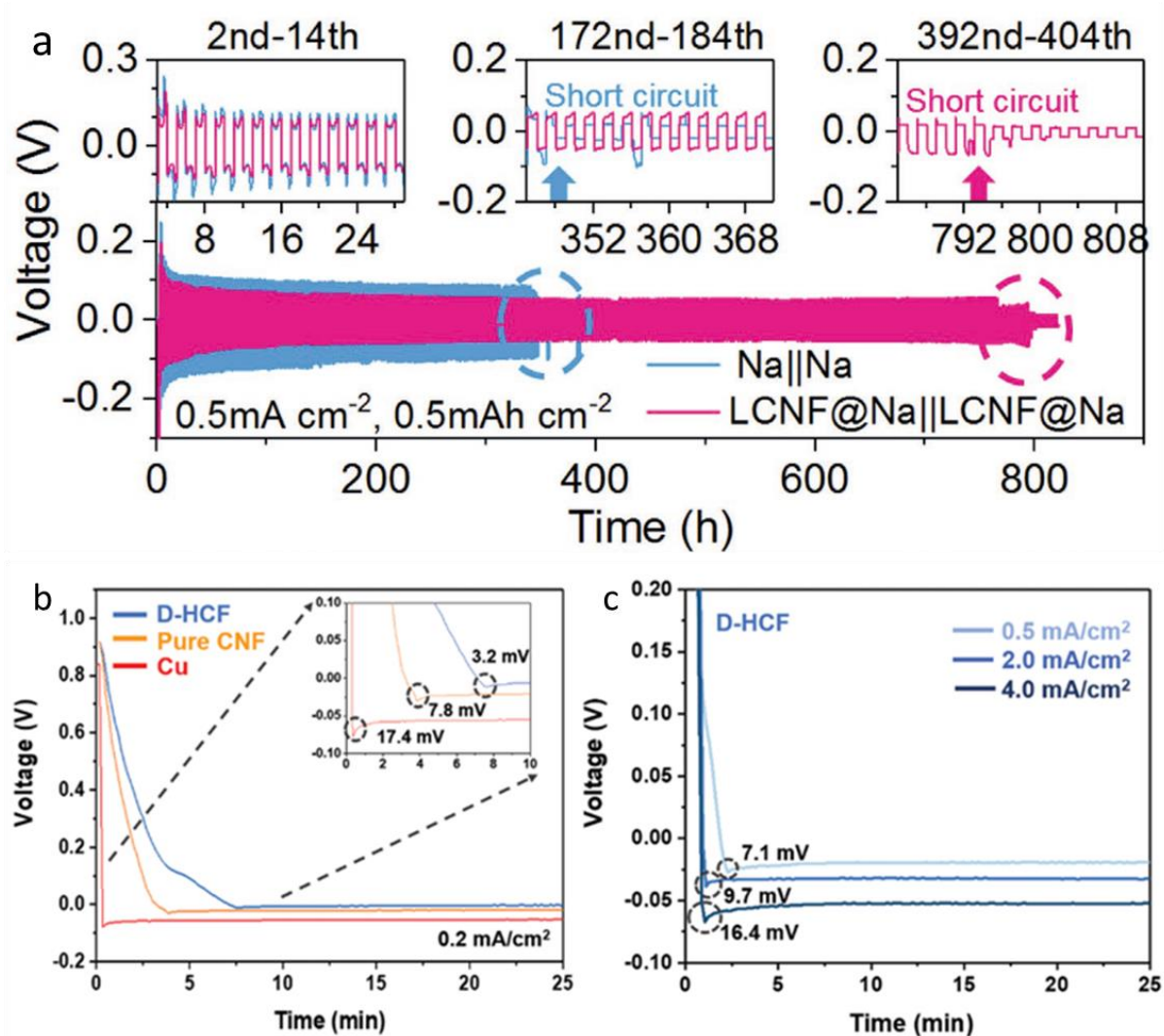


**Figure 1.6** a) Galvanostatic stripping/plating cycles of Na metal (blue) and Na-LCNF (pink) symmetric cells. Reproduced from ref. 47 with permission. Copyright 2016, Wiley. Voltage profile of Na metal electrodeposition on b) Cu foil, pure CF, and hetero-atom doped CF and c) on HCF at various current densities with the nucleation overpotentials highlighted in the grey circles. Reproduced from ref. 49 with permission. Copyright 2016, Elsevier Inc.

### 1.3. Liquid Electrolyte

Liquid electrolyte plays a large role in the stability and performance for Li based batteries. Responsible for the transportation of Li-ions between electrodes, forming the SEI, and characterizing the dendritic growth, the electrolyte system is an integral component of the battery

system. The morphology of the Li dendrites is dependent on the type of solvent present in the system. The two main types of non-aqueous solvents used in recent electrolyte development have been carbonate and ether based organic solvents. Carbonate based electrolytes, such as ethyl carbonate (EC), propyl carbonate (PC), ethyl-methyl carbonate (EMC), etc. will form “mossy” and needle-like growth<sup>35</sup> (Figure 1.7a), while ether based electrolytes, such as dimethoxy ethane (DME) and 1,3 dioxolane (DOL), will produce round, globule like growths (Figure 1.7b) The difference in dendritic morphology can be characteristic of the cycle life of the cell. Other factors such as composition and concentration of Li salts or electrolyte additives can modify the performance of the system through dendrite morphology characteristics, SEI formation and stability, and Li-ion transport efficiency.<sup>51–53</sup> In my project, I will explore the effect of solvents and electrolyte additives have on the cell performance with Li- and Na-CNF composite anodes and transition metal layered oxide cathodes.

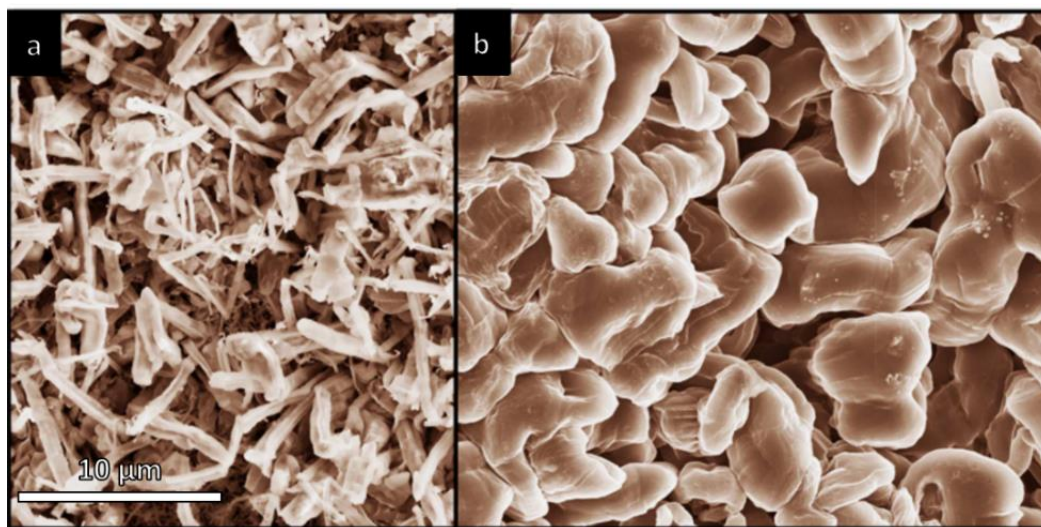


**Figure 1.7)** SEM images of Li metal dendritic growth on a Cu substrate containing the electrolyte system a)  $\text{LiPF}_6$ -PC having a thin, needle like dendrite morphology and b) 4M  $\text{LiFSI}$ -DME with a round, globular morphology with large surface. Reproduced from ref. 51 with permission. Copyright 2015, Springer Nature.

### 1.3.1 Carbonate-based electrolyte

Used in commercial systems, carbonate-based electrolytes have been a popular choice in recent research due to their high voltage window. Allowing the electrolyte system to sustain a charging profile of up to 4.5 V before experiencing unstable performance from decomposition by oxidation.<sup>54</sup> The high voltage window allows the system to use high energy density cathodes that requires high voltage, such as  $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$  (NMC) cathodes. Carbonate-based systems suffer from various side reactions with the polarized bare Li, thus forming a continuously thickening SEI layer as cycle number increases, decreasing overall performance, CE, and increasing the internal resistance. The categories for carbonate electrolytes are separated into cyclic and linear solvents. Linear solvents tend to be less stable and have lower CE with Li anodes, having higher reactivity and faster decomposition.<sup>52</sup> Cyclic solvents have higher CE from their reaction mechanism of their ring structure opening and forming a more flexible and stable SEI. EC, a popular solvent, can increase the CE of Li anodes up to 95%.<sup>19</sup> Linear and cyclic solvents are usually mixed in a 3:7 weight ratio because linear solvents enhance thermal stability and reduce the viscosity of the solution while cyclic solvents improve ionic conductivity, stability against lithium metal anode, and electrolyte stability at lower temperatures.<sup>55</sup> To enhance the performance of cells, small amounts of electrolyte additives are mixed with electrolyte solutions. Additives offer a wide range of modifications: altering the SEI composition, Li anode morphology and dendrite formation, improve thermal stability, etc.<sup>56-58</sup>

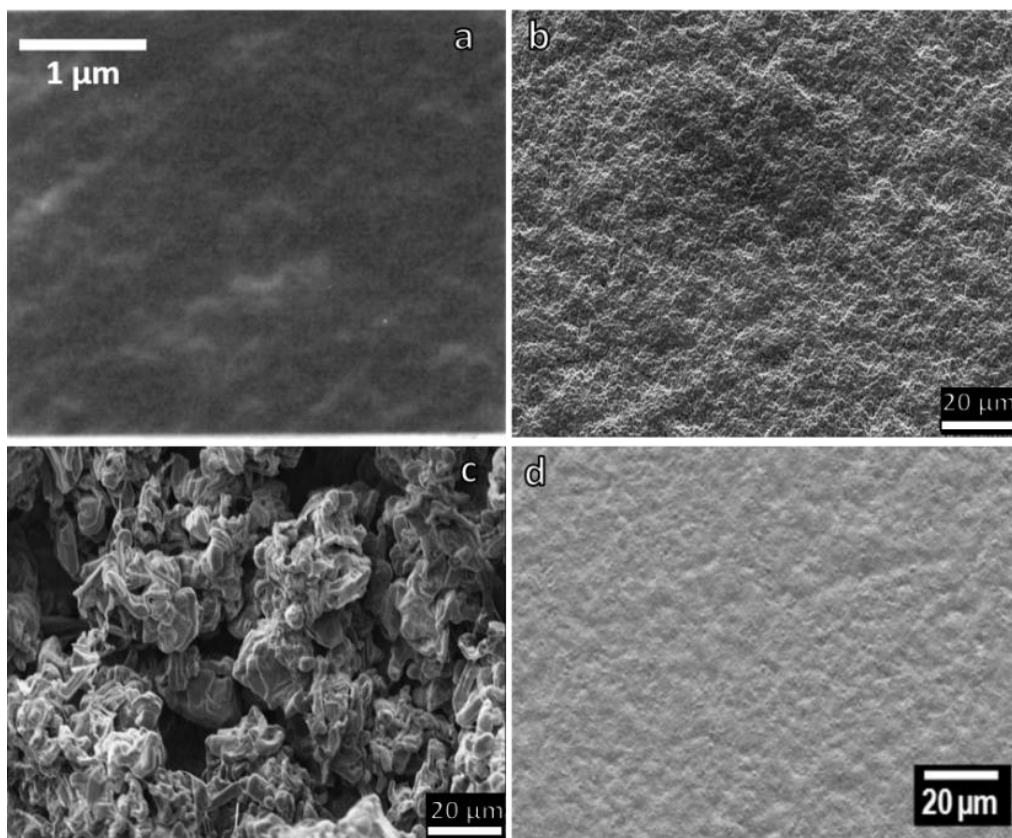


**Figure 1.8)** SEM images demonstrating the effect of the morphology of Li metal surface after cycling with electrolyte additives a) HF. Reproduced from ref. 60 with permission. Copyright 1996, IOP Publishing. b) VC c) FEC. Reproduced from ref. 52 with permission. Copyright 2013, IOP Publishing. d) CsPF<sub>6</sub>. Reproduced from ref. 62 with permission. Copyright 2013, American Chemical Society.

Negative side effects can occur if too much additive is added.<sup>59</sup> Hydrofluoric acid (HF) has been shown to smoothen the surface of Li metal and prevent dendrite formation (Figure 1.8a), but has not been used due to the dangerous nature of the acid.<sup>60</sup> Organic electrolyte additives, such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC) offer improved SEI stability via ring opening decomposition and easy polymerization.<sup>52</sup> VC adds more hydrocarbon compounds to the SEI allowing for polymerization and dendrite suppression. This polymerization increases the CE at room and elevated temperatures, but decreases at low temperatures.<sup>61</sup> FEC introduces more fluorine, forming LiF, contributing the inorganic layer of the SEI which is attributed to protection

of the Li surface from further reactions with the organic solvent. A more recent advancement comes from Ding et al.<sup>62</sup> showing that using certain metal cations allows for the formation of an electrostatic shield on the early stages of Li dendrite formation, where charge density is increased. The shield blocks Li attachment to the dendrite, and prevents the dendrite from continuous growth and forces Li ions to plate around the dendrite forming a smooth dendrite-free morphology.<sup>62</sup>

### 1.3.2 Ether-based electrolyte

Ether-based electrolyte systems are also used due to their increased stability against polarized lithium and having less side reactions, resulting in high cycle life. The improvements in cycle performance can be attributed to the formation of a stable SEI and the change in morphology for dendritic growths. Ether electrolytes produce round dendrites with large surfaces (Figure 1.8b), minimizing the risk of dendrites piercing through the separator and causing possible short circuit of the cell. These systems are used primarily in Li-S batteries and with low voltage cathodes, due to the low voltage limitations of the electrolyte. Most recent research efforts use the combination DOL/DME for its high stability and long cycle life.<sup>40,63,64</sup> Recently, a new ether combination, 1,4 dioxane (DX)/DME was revealed that had a much higher voltage stability window than the regular ether electrolyte at ~4.8V.<sup>65</sup> DX offers a much higher voltage stability to the electrolyte mixture, compared to DOL/DME (~4V). This mixture allows for higher voltage cathode possibilities for ether-based electrolytes without the risk of rapid decomposition of the electrolyte.

Li-S batteries suffer from poor CE and cycle performance when paired with organic electrolytes from the formation of lithium polysulfide species ( $\text{Li}_2\text{S}_n$ ,  $n=2-8$ ) that are soluble in organic electrolytes.  $\text{LiNO}_3$  is one of the most prominent additives for Li-S ether systems. The addition of  $\text{LiNO}_3$  forms a protective layer on the anode surface to stabilize the Li anode and protect the Li anode from reacting with polysulfide species via reduction of insoluble  $\text{Li}_x\text{NO}_y$

species which oxidize the polysulfide species and prevents the redox shuttle of lithium polysulfides<sup>66,67</sup> The addition of phosphorous pentasulfide ( $P_2S_5$ ) has been shown to also suppress the polysulfide shuttle and improve the discharge capacity and capacity retention.<sup>68</sup>  $P_2S_5$  modifies the Li anode surface to have a dense passive layer, blocking the pristine Li layer from the formation of polysulfide and eliminating the polysulfide shuttle. A mixture of  $LiNO_3$  and  $P_2S_5$  has a synergistic effect to have a smooth plating on Li anode without formation of dendrites.  $LiNO_3$  forms the protecting passive layer on the surface of lithium metal anode and  $P_2S_5$  reacts with the polysulfide compounds to form insoluble  $LiS/LiS_2$  compounds on the top layers of the SEI preventing the polysulfide shuttle and electrolyte decomposition, decreasing loss of active sulfur and increasing cycle life.<sup>66,69</sup>

### **1.3.3 Solvent-in-salt electrolyte**

Recent studies have started experimenting with using high concentrations of Li salts in ether solvents to improve the anode's performance and stability. By increasing the salt-to-solvent mole ratio, the conductivity of the electrolyte decreases, but the voltage stability increases, decreasing electrolyte decomposition.<sup>70</sup> Ionic conductivity is a function of viscosity and Li-ion mobility. By reducing the amount of free solvent and increasing the Li-ion concentration, there is an increase in the solvent's reductive stability and Li plating/stripping efficiency.<sup>51</sup> The high concentration of Li salt allows for Li-ion to migrate through the electrolyte faster and shortens the distance necessary for Li reduction at the electrode surface. These characteristics allow for stable cycling of Li metal anode at high current density rates. A salt-in-solution (SIS) study using 4M LiFSI in DOL/DME solvent allows stable cycling at high current density and with good CE.<sup>51</sup> The Li anode stability is attributed to stable SEI formation preventing excessive electrolyte decomposition, resulting low impedance and good cycle life. While the SIS method provides

improved cycling performance and cycle life, with Li salts at 1M concentration costing ~6% of total battery components, increasing the concentration of Li-salts are costly and not optimal for commercialization.

#### **1.3.4 Boron-salt electrolytes**

Borate salts have been shown to be a promising candidate for Li and Na electrolytes due to their good electrode stabilization properties. The electrolytes containing these borate salts have been reported to have improved cycling Coulombic efficiency, thermal stability, and helps form a more robust electrode-electrolyte interphase that helps result in better overall cell stability.<sup>71-76</sup> However, these salts often have lower solubility in carbonate solvents due to having a stronger association between the Li and Na cation and the borate anion resulting in a higher viscosity and lower ionic conductivity in the electrolyte.<sup>73</sup> The smaller ionic size of the boron results in a stronger ionic coordination and typically reduces the dissociation between the alkali metal cations and borate anions.<sup>73,74,77</sup> Borate salts were first incorporated as an alternative for Li and Na hexafluorophosphate ( $\text{PF}_6$ ), one of the most widely used salts in Li and Na ion battery research and in modern commercialized Li ion batteries. Li- and  $\text{NaPF}_6$  is commonly used due to its high solubility in carbonate solvents, good ionic conductivity, and wide electrochemical voltage window.<sup>73,74,77</sup> However, Li- and  $\text{NaPF}_6$  have poor reductive and elevated thermal stability and easily undergoes hydrolysis to yield undesirable products such as  $\text{PF}_5^-$  which can further react to make Hydrofluoric acid (HF).<sup>72,73</sup> The presence of HF is well known for causing particle degradation and transition metal dissolution in cathode materials and being corrosive to the Al current collector.<sup>72,73</sup>

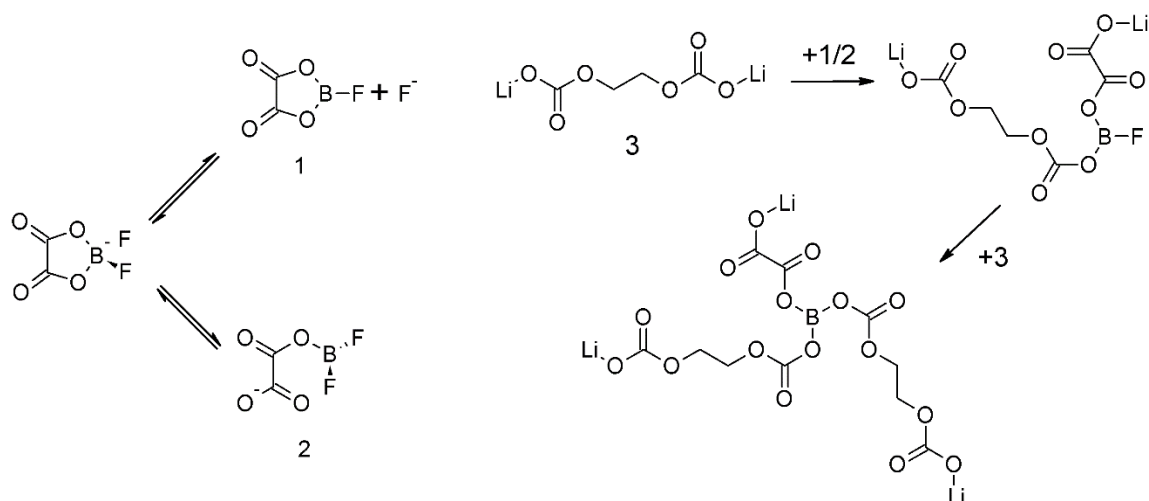


**Figure 1.9** Proposed decomposition reaction pathway of the DFOB anion oligomerization process.

Two widely studied borate counter ions for Li and Na batteries are tetrafluoroborate ( $\text{BF}_4$ ) and difluoro(oxalato)borate (DFOB). While Li and  $\text{NaBF}_4$  electrolytes have shown poor ionic properties for a single salt electrolyte, the use of the  $\text{BF}_4$  as an electrolyte additive with other electrolytes, such as Li- and  $\text{NaPF}_6$ , has improved passivation on the surface of cathode particles and on the Al current collector used in cathode electrodes and has improved cycling stability.<sup>75,78</sup> The investigation of DFOB as a single salt electrolyte, or as an additive, has shown more promising results in both Li and Na battery studies. The DFOB anion undergoes a ring-opening decomposition pathway which can go through an oligomerization process and form a strong oligomer network in the passivation layer on the cathode surface and protect the cathode particles from further reactions with the electrolyte (Figure 1.9).<sup>77,79–81</sup> Previous reports in the literature have shown via NMR analysis that the DFOB salts are more hydrolytically stable in the presence of water in the solvent and HF formation was not observed, unlike in  $\text{PF}_6$  and  $\text{BF}_4$  electrolytes. In anode free cells, the combination of  $\text{LiDFOB}$  and  $\text{LiBF}_4$  showed the greatest improvement to the cell's cycle life than with either salt mixed with  $\text{LiPF}_6$  (Figure 1.10).<sup>76,82</sup> The enhanced cathode and anode stability observed through the use of these boron based salts show promising results for utilization, in some configuration, for

future research. However, the current literature on the sodium side is lacking in comparison to the more historied investigation into the lithium salts and will require more testing and analysis.

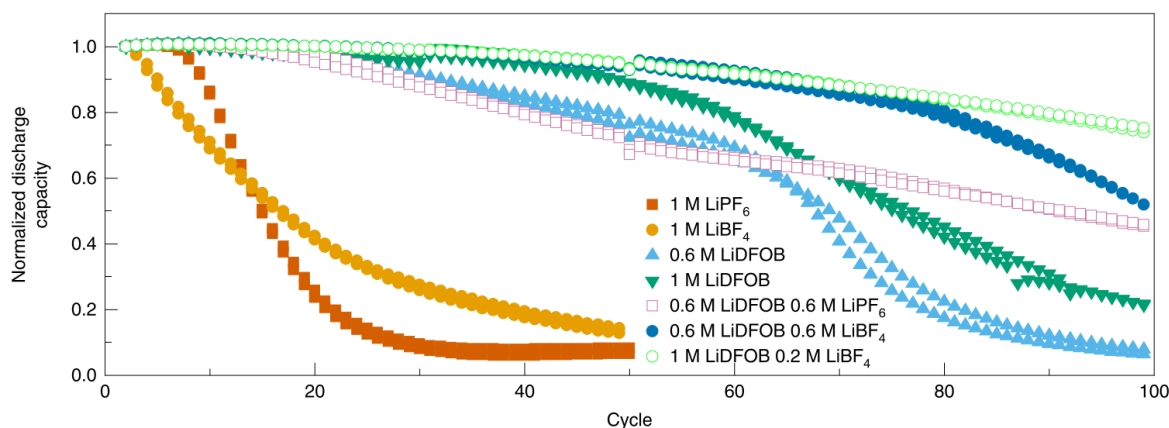


**Figure 1.10** Discharge capacity retention versus cycle number for anode-free pouch cells with single- and dual-salt electrolytes with  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ , and  $\text{LiDFOB}$ . Reproduced from ref. 76 with permission. Copyright 2019, Springer Nature.

## 1.4 Solid Electrolyte Interphase

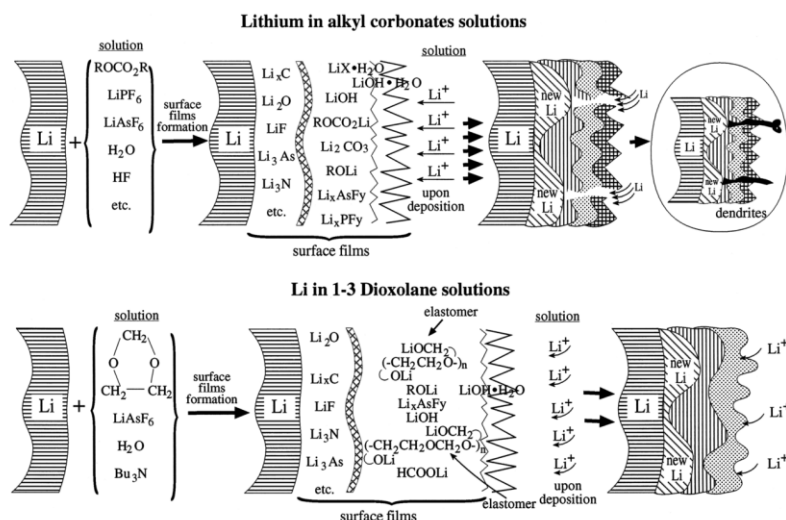


**Fig 1.11.** Diagram demonstrating the composition of the SEI that can be observed in carbonate and ether based electrolyte systems.<sup>83</sup> Reproduced from ref. 83 with permission. Copyright 2000, Elsevier Inc.

The term and conception of the SEI was first named so by E. Peled in 1979, describing how Li reacts with the electrolyte to form a protective layer, preventing further reaction of the

electrolyte with lithium.<sup>84</sup> The SEI has a dual function to transport lithium cations, in addition to protecting the anode.<sup>85</sup> SEI composition has been studied extensively using X-ray photoelectron spectroscopy (XPS). There are two main layer types that comprise the SEI, the organic phase, containing ROLi, Li<sub>2</sub>CO<sub>3</sub>, ROCO<sub>2</sub>Li, etc. and the inorganic phase, LiX, Li<sub>3</sub>N, Li<sub>2</sub>O, etc (Figure 1.11).<sup>59</sup> The composition of the SEI helps with the stability of Li based anodes, as well as suppression of dendritic growth. If the SEI layer cannot adjust to the volume changes of the Li anode it can fracture, allowing for more electrolyte to react with the fresh lithium. The resilience of the SEI is related to the impedance of the cell performance as well. If the SEI breaks and allows further electrolyte consumption, a thicker SEI layer will be formed, increasing the resistance in the cell and negatively impacting Li-ion migration to and from the anode surface.<sup>86</sup> Determining the composition and the function of the components of the SEI is a crucial necessity to improve the performance and stability of lithium based anodes and secure their position for the next-generation of commercialized secondary batteries.

#### **1.4.1 Characterization of SEI**

The composition of the SEI is dependent on the composition of the electrolyte and cycling history. The solvent, Li-salts, and electrolyte additives play a large role in the formation, structure, and performance of the SEI. As seen in Figure 1.11, the compounds present in the SEI differ based on the electrolyte used.<sup>87</sup> There are multiple techniques that allow for the characterization of the composition and performance of the SEI. Utilizing XPS, the structure of the SEI can be investigated. Using X-rays of known energy, the determination of the species present within the SEI can be discovered by its binding energy (BE). The BE is the difference between the X-ray energy and the Kinetic Energy (KE) of the photoelectron released from the species. The energies can be tuned for specific species that are known to be in the SEI, via electrolyte composition. The

determination of the SEI composition is necessary to understand the performance and functionality of the SEI layer that is present on the anode surface. Multiple studies have been performed to determine the effect on various salts, solvents, and electrolyte additives have on the SEI composition, Li anode performance, and morphology.<sup>52,51,85,58</sup>

The stability of the SEI, and the performance of the electrolyte system, can be determined through electrochemical and impedance investigations.<sup>86,88</sup> Measuring the change in voltage profiles in Li-Li symmetrical cells during plating/stripping cycles gives insight to the performance of the electrolyte and the SEI that is formed. Increase in voltage in overpotential profiles correlates to an increase in internal resistance within the cell system and is attributed to electrolyte degradation and continuing SEI formation, resulting in a thick passivation layer. The electrolyte ionic conductivity and electrode surface resistance can be investigated by coupling the electrochemical testing with impedance spectroscopy. Impedance profiles allow for the distinction if the resistance is due to charge transfer or mass transfer limitations. Researchers have used these methods to determine the stability and performance of multiple electrolyte systems to study the stability of the resulting SEI.<sup>88,59</sup>

#### **1.4.2 Artificial SEI**

A newer approach to assist the SEI, in anode stability, is the formation of an artificial SEI. Artificial SEIs are functionalized to coat and protect the Li anode from excessive electrolyte decomposition and help with Li-ion mitigation. Artificial SEIs can also create a high-pressure barrier to prevent dendritic formation by increasing the sheer modulus for Li deformation. Reacting the lithium foil with certain compounds will form the artificial SEI and determine its supportive properties. Using  $\text{Al}_3\text{I}$ , the formation of a Li-Al and Li composite is formed on the anode, forming a stable layer, preventing dendrite formation and increasing the anode's cycle life

and CE.<sup>89</sup> The use of tetraethoxysilane has also been shown to form a stable protective layer against electrolyte decomposition and limiting growth of impedance in subsequent cycles.<sup>90</sup> The use of gases to pre-treat the lithium, such as N<sub>2</sub> and acetylene, have been shown to form protective Li<sub>3</sub>N and polyacetylene coatings on the surface of Li metal anode.<sup>91,92,93</sup> More recently, there has been the use of atomic layer deposition (ALD) to deposit a layer straight onto the Li anode surface with better control of the layer's thickness, uniformity, and decrease in defects, disregarding the need for precisely controlled chemical reactions. Kozen et al. shows that depositing an Al<sub>2</sub>O<sub>3</sub> layer on the surface of lithium metal protects the anode from air and electrolyte corrosion. The ALD layer shows improved cycle life, CE, and dendrite suppression, with a smoother Li surface morphology, compared to bare Li metal anode, after 100 charge-discharge cycles (Figure 1.12).<sup>63</sup>

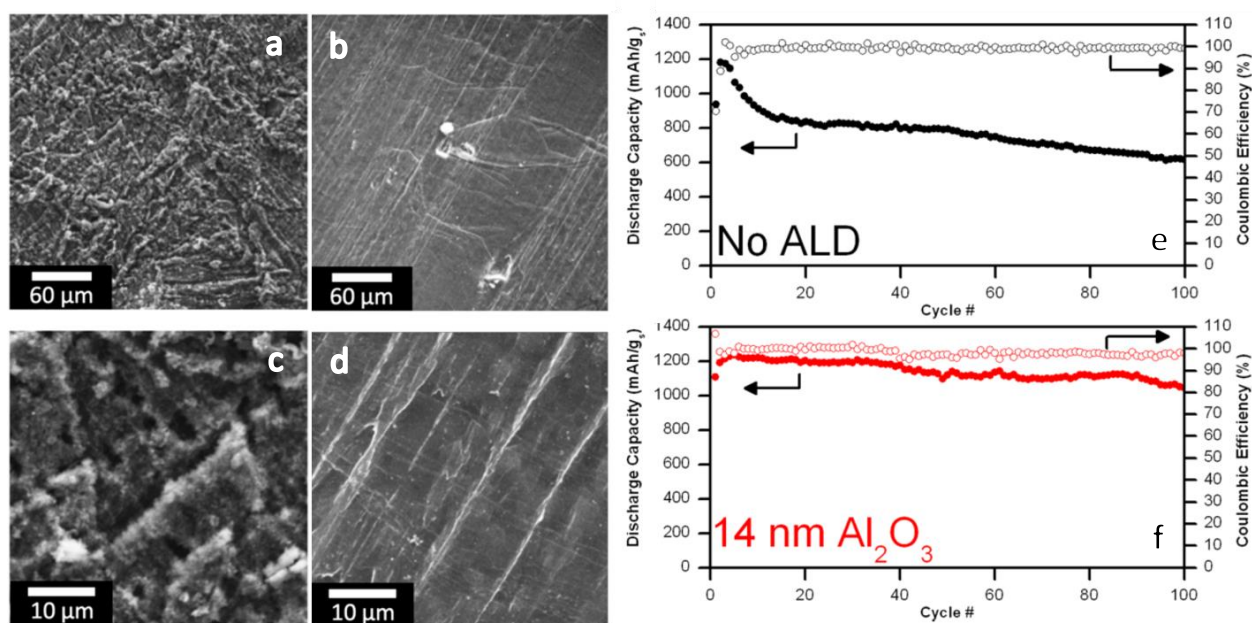


**Figure 1.12** SEM images of (a,b) unprotected Li metal after exposure to DME/sulfur solvent for 7 days and (c,d) Li metal protected with Al<sub>2</sub>O<sub>3</sub> artificial SEI after exposure DME/sulfur solvent for 7 days. Electrochemical profile (e,f) showing the discharge capacity retention and CE of LMA with and without Al<sub>2</sub>O<sub>3</sub> coating. Reproduced from ref. 63 with permission. Copyright 2015, American Chemical Society.

An issue pertaining the artificial SEI consists around the fact that the protective layer is from pre-battery treatment, and if the artificial SEI layer cracks, or begins to deteriorate, another protective layer is unable to be reformed, leaving the Li anode unprotected to electrolyte decomposition, cracking, and dendrite formation. The conditions of the artificial SEI formation must be precisely controlled to achieve a stable and functional layer to protective the Li anode.

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## 2. Understanding the Critical Chemistry to Inhibit Lithium

### Consumption in Lean Lithium Metal Composite Anodes

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#### 2.1 Abstract

Lithium metal has been deemed by many as the “Holy Grail” of anode materials due to its high theoretical capacity (~3860 mAh/g), having a redox potential (-3.040 V vs SHE), and being lightweight. The goal of this work is to investigate the relationship between a lean lithium metal anode and its consumption as a function of host materials, electrochemical protocol, and electrolyte composition. With the use of carbon nanofibers, lithium metal has been electrodeposited into the host matrix and used in a battery with the  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  cathode. The mass-loading of lithium can be easily controlled and utilized to investigate the practicality of an anode limited battery (i.e., limited lithium with an effective thickness < 15  $\mu\text{m}$ ) in a high surface area matrix. We quantify the consumption rate of active lithium using different electrolyte additives and current rates in full cells and observe that the lithium consumption behavior in an anode-limited cell is different from that in an anode-excess cell. Our results highlight the necessity of applying truly lithium-limited cells when evaluating the electrochemical properties of lithium anodes and electrolyte additives. By extending this method to a standard graphite host, full cells can retain 75% of initial capacity after 1,000 cycles. The present study demonstrates the importance of graphitic carbon in increasing the lifespan of limited lithium (< 15  $\mu\text{m}$ ) for practical lithium metal batteries.

## 2.2 Introduction

Next-generation energy storage technologies call for materials and manufacturing that can deliver batteries with higher energy/power density and improved safety to meet the demanding applications. Lithium ion batteries are one of the most popular energy storage solutions and will continue dominating consumer electronics and vehicular applications. Currently, there is need to establish methods to concurrently improve the electrochemical properties of individual cell components, particularly the cathode, anode, and electrolyte. The central goal of these methods is to increase the practical capacity of electrode materials, widen the operating voltage window of electrolyte and elevate the cell voltage. To date, a number of new or renovated strategies are developed to improve the anode chemistry. For example, alloying-type (e.g., Si) and deposition-type (e.g., Li metal) are the most promising anode chemistries of choice for next-generation lithium ion batteries. In particular, lithium metal is considered the “holy grail” of battery technologies and has been intensively studied. However, the lithium metal anode was discouraged in early days due to inferior characteristics such as lithium dendritic growth and poor Coulombic efficiency (CE).<sup>1</sup> In recent years, the rapid development of solid-state electrolytes has spurred revisiting lithium metal anodes. Recent studies, however, seemed to inform that solid-state electrolytes are a necessary but not a sufficient condition for implementing lithium metal anodes.<sup>52–55,56</sup> Operating lithium metal anodes in organic liquid electrolytes (often with additives) can be a viable option for upgrading the state-of-the-art “graphite/electrolyte/cathode” commercial chemistry.<sup>22,31,57,36,58</sup> One can expect that such an upgrade would require minimal changes of current battery manufacturing infrastructures and could be the near-term solution to improve battery technologies. If successfully done, we expect that beyond lithium ion batteries such as lithium-sulfur batteries and lithium-

oxygen batteries can be practically possible, albeit there are numerous cathode challenges associated with these chemistries.

To date, lithium metal anodes are still handicapped by the challenges that were identified several decades ago, including but not limited to lithium dendritic and mossy growth, unstoppable side reactions between lithium metal and electrolytic solution, and poor CE. These challenges are associated with the thermodynamic nature of lithium metal and difficult to be completely resolved. However, sufficiently slowing down the kinetics of these processes can help achieve required cycle life for practical applications. Recent studies towards this direction have shown some promising success examples. For example, modifying lithium metal surface morphology<sup>13,14</sup>, using carbonaceous host materials<sup>17,18,20</sup>, modified separators<sup>59,60</sup>, SEI modifications<sup>61,62</sup>, electrolyte modifications<sup>21,40,63</sup> etc. Most of these studies utilize lithium foil or high-mass loading lithium as the anode. In a practical cell, however, requirements of high energy density and desired safety characteristics necessitate limiting the mass loading of lithium metal anodes.<sup>55</sup> The electrochemical behavior of a bulk lithium foil can be drastically different from that of a lithium thin film (e.g., tens of microns that is needed for a practical cell). Furthermore, depositing metallic lithium onto the anode current collector involves infinite relative volume expansion, and the deposited lithium metal has a higher specific surface area than the pre-existing lithium metal anode. In cells with bulk lithium anodes what most lithium anode studies base on, these factors are unlikely to play a major role in determining the full-cell performance, especially within a limited number of cycles. For example, it is common to cycle Li-NMC half cells for hundreds of cycles without the need of considering the consumption of bulk lithium metal anode (i.e., infinite supply of fresh lithium metal).<sup>64</sup> In contrast, in practical cells with limited lithium loading (e.g., thin-film

lithium,  $\leq 30\text{ }\mu\text{m}$ ), these factors can greatly impact the availability of lithium reservoir and thus determine the cycle life of lithium metal batteries.<sup>65,66</sup>

Herein we studied the electrochemical properties of the lithium metal anode under anode-limited conditions (limited lithium loading on carbon nanofibers with low-concentration graphitic carbon). We observed that the lithium metal anode was consumed by electrolytic solution continuously upon cycling, although certain electrolyte additives were capable of slowing down the consumption. We quantified the rate of lithium consumption as a function of electrolyte additive and charging-discharging rate and found that a bulk lithium metal failed to represent the electrochemical properties of a thin-film lithium anode. However, when loaded on graphite, the lean lithium anode could sustain much longer cycling (75% capacity retention after 1,000 cycles), indicating the importance of a strong lithium-support interaction. Our study offers new insights into the electrochemical properties of lithium metal anodes and highlights the importance of considering the form factor (limited lithium loading *versus* bulk lithium) in designing practically viable lithium metal batteries. Finally, the methodology reported herein can be applied to study other anodes such as sodium, magnesium, and aluminum.

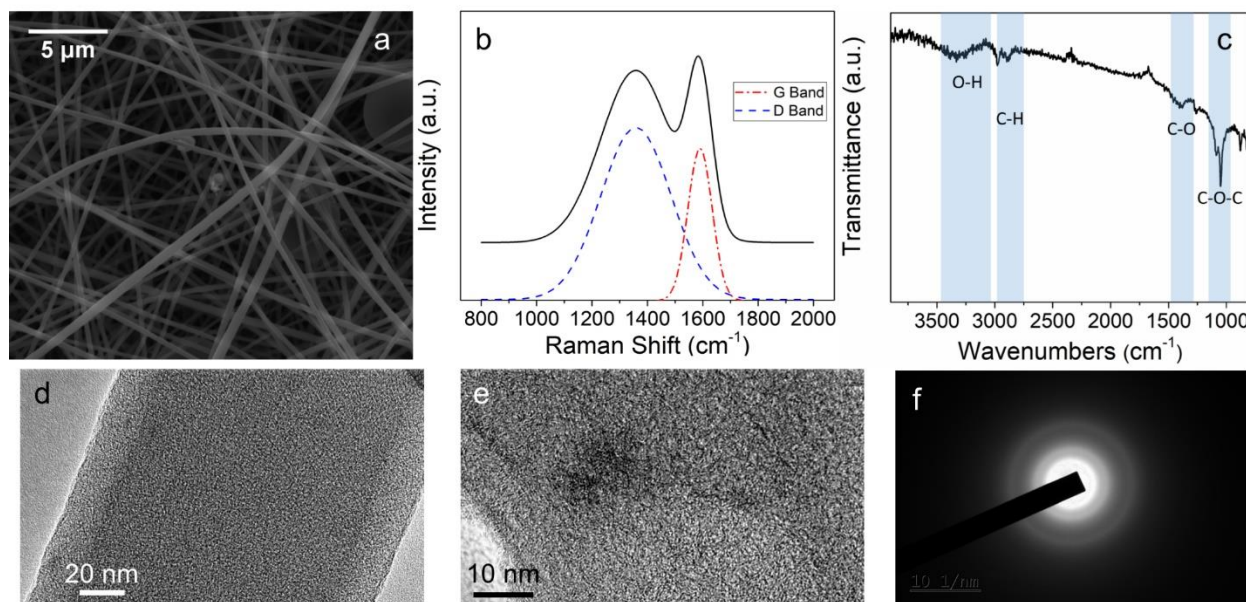


**Figure 2.1) Characterization of pristine CNF** (a) SEM image of the pristine CNF porous matrix structure, (b) Raman spectrum of the pristine CNF, (c) FTIR spectrum of the pristine CNF, (d-e) TEM images of the pristine CNF at two different magnifications, and (f) electron diffraction pattern of the pristine CNF showing the amorphous characteristics of the CNF.

## 2.3 Results and Discussion

### 2.3.1 Characterization of carbon nanofiber

Figure 2.1a shows the smooth surface of the pristine carbon nanofibers (CNFs) and their porous and interwoven structure. The spheres in the CNF matrix were due to the electrospinning process, forming droplets in the carbon fiber matrix that were unable to be converted to CNF. Similar results have been reported in the literature.<sup>67</sup> To determine the functionalization and chemical composition on the pristine CNF, Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were utilized (Figures 2.1 b-c, Figure S2.1). Raman spectroscopy (Figure 2.1b) shows that the CNF had a more prominent disorder band structure (1200-1500  $\text{cm}^{-1}$ ) than graphitic structure (1500-1700 $\text{cm}^{-1}$ ). As seen in

Figure 2.1c, there is a stretch between 3200-3500  $\text{cm}^{-1}$  indicating the presence of  $-\text{OH}$  group, possibly due to water adsorption on the surface of the fibers or inherent  $-\text{OH}$  functionalization on the surface of the fiber<sup>18</sup>, followed by  $\text{sp}^3$  alkyl  $-\text{CH}$  peaks around 2980  $\text{cm}^{-1}$ . Epoxy ( $\text{C}-\text{O}-\text{C}$  1045  $\text{cm}^{-1}$ ) and  $\text{C}-\text{O}$  (1386  $\text{cm}^{-1}$ ) were also present within the surface structure of the nanofiber.<sup>18</sup>  $\text{C}1\text{s}$  XPS shows the presence of the  $\text{C}-\text{C}$  bond at 284.8 eV (Figure S2.1). The transmission electron microscopy (TEM) and electron diffraction results showed that the resulting CNF exhibited low crystallinity and nearly amorphous structure (Figures 2.1d-f). This initial characterization results can provide insight into the chemical properties of the CNF and allow us to study the relationship between the carbon chemical environment and the performance of the lithium/carbon composite anode.

### 2.3.2 Electrodeposition of Li-CNF composite anode

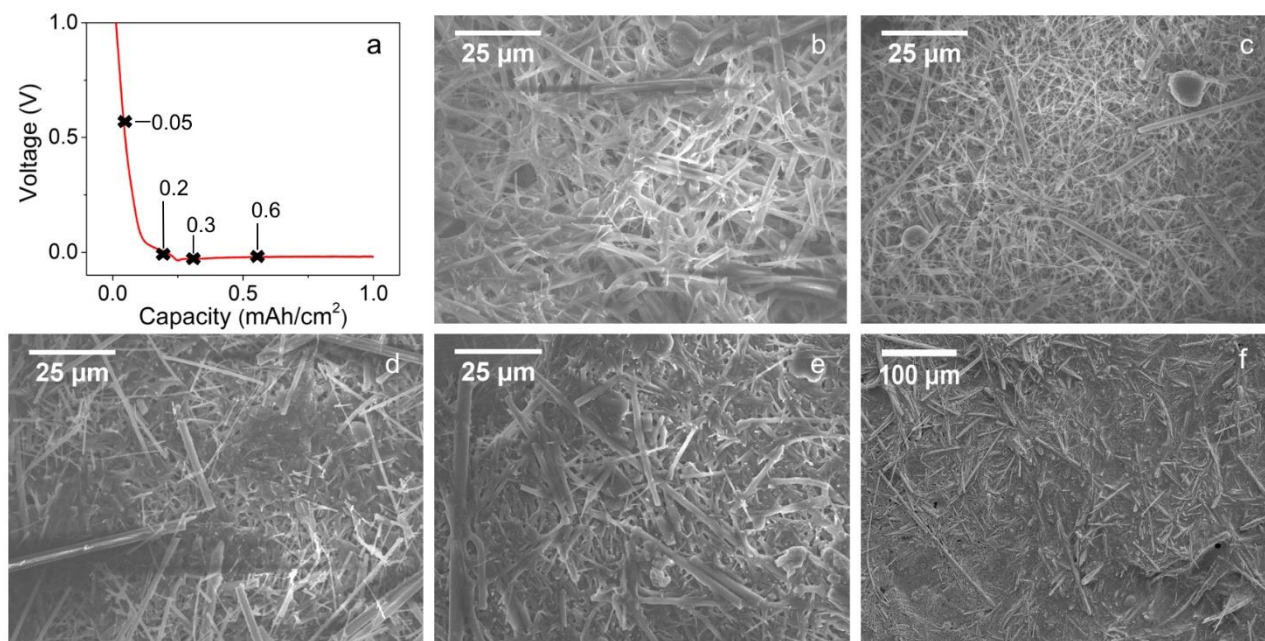


**Figure 2.2)** (a) Voltage profile of electrodeposition of 1mAh/cm<sup>2</sup> areal capacity Li (ca. 4.8  $\mu\text{m}$  effective thickness) using 1M  $\text{LiPF}_6$  in EC/EMC with a current density of 0.05mA/cm<sup>2</sup> and corresponding SEM images taken during increasing stages of deposition at (b) 0.05mAh/cm<sup>2</sup> (c) 0.2mAh/cm<sup>2</sup> (d) 0.3mAh/cm<sup>2</sup> and (e) 0.6mAh/cm<sup>2</sup>. With (f) showing low-magnification image after 1mAh/cm<sup>2</sup> deposition with addition of 2% VC. Remnants of glass fiber can be seen imbedded in the deposited lithium metal.

Electrodeposition was utilized as the method to impregnate lithium metal into the CNF matrix (procedure in experimental details). Multiple points in the deposition profile were chosen to observe lithium insertion and growth within the CNF. The first point (Figure 2.2b), having a total areal capacity of  $0.05\text{mAh/cm}^2$  shows the initial seeding of the Li metal. Figure 2.2c, at  $0.2\text{mAh/cm}^2$  has the discharge voltage first crossing the threshold of 0V, which has been shown to start the nucleation process of metallic lithium.<sup>19</sup> At  $0.3\text{mAh/cm}^2$  (Figure 2.2d) the growth phase of metallic lithium began and shows the fast growth of the lithium seeds into conglomerates of metallic lithium. The last point (Figure 2.2e) at  $0.6\text{mAh/cm}^2$  shows the continuation of the growth of the lithium conglomeration, beginning to coat the carbon fibers. The surface morphology of the CNF after deposition changed, transforming from the smooth surface of the CNF, into one that was rough and covered with lithium (Figure S2.2). Remnants of the glass fiber separator can be seen in all of the SEM images and is assumed to not affect the performance of the Li/CNF composite anode. Furthermore, we conjectured that after the lithium deposition the porous carbon nanofibers were filled with metallic lithium as well as organic residuals from electrolyte decomposition.

The composite anodes were retrieved after electrodeposition and combined with  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  composite cathodes to test as full cells and cycled at a 1C current rate between 2.5 V and 4.5 V. The resulting data was normalized to have the first discharge capacity be 100% of active lithium available and have the fading primarily attributed to the anode. A coin cell composing of an excess bare lithium foil following same cycling parameters was added as the control. An excess amount of electrolyte was used in all systems to rule out electrolyte decomposition as a factor to the fading cycle life within 100 cycles. The cell lifespan of the

composite anode with no electrolyte additives (NA) cycled at a 1C rate failed immediately in subsequent cycles, as seen in Figure 2.3a (“1mAh/cm<sup>2</sup> NA”), showing a drastic fade in capacity. The anode had an initial CE of 89.13% which suddenly dropped to 74.97% within the next cycle (Figure S2.3a), and the specific capacity fading from its initial 156.1 mAh g<sup>-1</sup> to 28.3 mAh g<sup>-1</sup> within 10 cycles (Figure S2.4). Initial active lithium was lost due to side reactions between Li and electrolyte to form the SEI layer. The quick capacity fading can be attributed to having a lean anode system, with the anode only having 1mAh/cm<sup>2</sup> (4.8 μm effective thickness) total areal capacity of deposited lithium. To improve performance, a 2% (by weight) vinylene carbonate (VC) electrolyte additive solution was made, due to the reported benefits that VC can add to SEI formation, CE increase, and cycle life improvements.<sup>31,22</sup> Electrodeposition was performed with the electrolyte containing VC as well. We hypothesize that it formed a stable SEI layer on the composite anode during deposition via the decomposition and polymerization of VC.<sup>2,22</sup> SEM was taken for the composite anode after the 1mAh/cm<sup>2</sup> deposition with VC (Figure 2.2f) showing a slight difference between the morphology of the lithiated CNF with and without the addition of VC.

### 2.3.3 Full Cell Measurements

The composite anode with VC had an areal capacity of 1mAh/cm and was cycled at a 1C current rate. The cycling performance was improved, having an initial CE of 90.01% for the first cycle and improving to ~99% for the next 10 cycles (Figure S2.3c). The discharge profile followed the same voltage curve throughout the life of the anode showing an insignificant increase of hysteresis and having stable anode performance (Figure S2.5). After 13 cycles, the system started to exhibit fast drops in capacity, while still following the same discharge voltage curve. The

discharge profile began to show “knee”-like dips having sudden, sharp drops in voltage, followed by a small plateau, and resuming to regular discharge behavior (Figure S2.5).

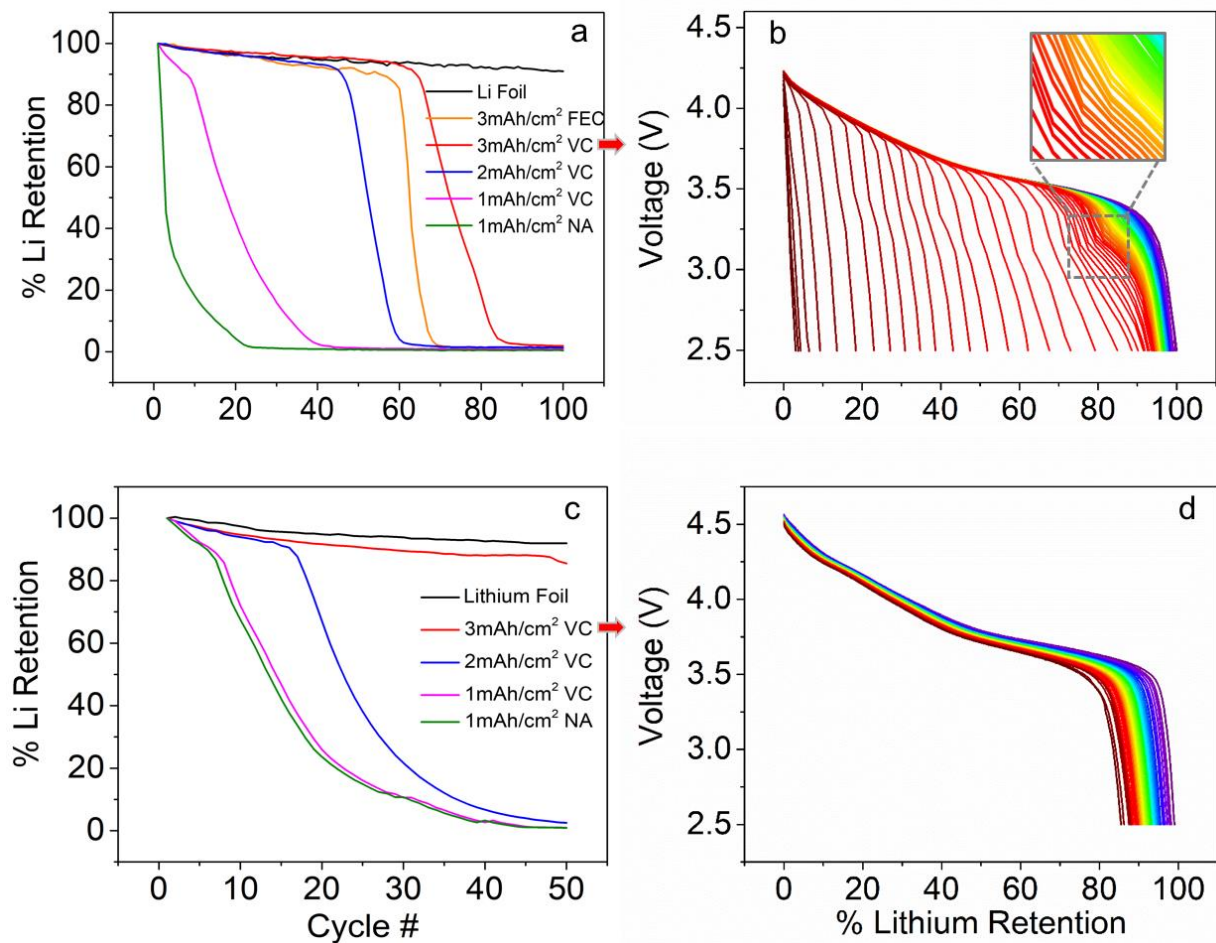


**Figure 2.3)** Lithium retention graphs of Li/CNF composite anodes retention profiles for (a) 1C cycling rate for varying deposition capacities and electrolyte additives including 2% vinylene carbonate (VC) and 2% fluoroethylene carbonate (FEC) followed by the (b) discharge profile for 3 mAh/cm<sup>2</sup> composite at 1C rate (2.5 - 4.5V) showing the transition from the compact discharge profile to degradation of lithium retention and the “knee” that develops at the beginning of anode destabilization and causing rapid cell failure. Composite anode retention for (c) C/10 (2.5 - 4.6V) cycling profile and (d) discharge profile for 3 mAh/cm<sup>2</sup> composite at C/10 rate. The NA in the figure represents “no additive was added during lithium deposition”.

The fading between neighboring discharge cycles was uniquely uniform after the initial stable cycling of the anode. This phenomenon is rarely seen and not well understood in literature, and we theorize it to be due to having a lean lithium composite anode. The amount of active lithium within the anode is depleted, causing fast, consistent drops in capacity and performance, which we

deem the state of rapid cell failure (Figure 2.3a). We believe that we might be able to quantify the amount of lithium that is being consumed per cycle. To test this hypothesis, we increased the capacity of the composite anode to  $2\text{mAh/cm}^2$  ( $9.6\text{ }\mu\text{m}$  effective thickness) and  $3\text{mAh/cm}^2$  ( $14.5\text{ }\mu\text{m}$  effective thickness) (Figure 2.3) to determine the rate of lithium consumption in the Li/CNF composite anode. As seen in Figure 2.3a, the stable cycling before the sudden capacity fading for the  $2\text{mAh/cm}^2$  and  $3\text{mAh/cm}^2$  cells were, at 46, and 66 cycles of stable cycling between 99.5-99.9% CE (Figures S2.3e-g), with low hysteresis, before the start of rapid cell failure. To test the robustness of this method, the  $3\text{mAh/cm}^2$  Li/CNF composite anode was remade and cycled. The anodes all show similar performance with around  $\pm 5$  stable cycles with  $\sim 99\%$  CE before the active lithium becomes consumed, and followed the same discharge profile characteristics, including the rapid and equal drop in discharge capacity (Figure S2.6). To ensure that the fade in capacity was not primarily due to the cathode, we retrieved a cathode from a cell after reaching the state of rapid cell failure. The cathode was reused in a new cell with a fresh lithium metal anode, the capacity returned to a high capacity and maintained high CE and cycling stability for over 150 cycles (Figure S2.7). We concluded that the quantification of lithium consumption for stable cell cycling at 1C to be  $\sim 20\text{-}23$  stable cycles of 99% CE per  $1\text{ mAh/cm}^2$  of lithium deposited, with 2% VC, after the threshold of initial lithium consumption.

The initial low hysteresis and compact capacity retention can be attributed to the formation of a stable SEI from the VC decomposition during electrodeposition, forming a stable layer to help prevent the initial consumption of lithium during the first cycles. The flexible carbon matrix attributes to the good performance by accommodating and minimizing effect of the lithium's relative infinite volume expansion during the plating/stripping cycles. The initial SEI formation

and benefit from the carbon matrix assist the composite anode to have similar initial capacity retention and CE to that of a full cell with an excess lithium metal anode and same cell parameters.

To investigate the effect that cycling rate has on the performance of the composite anode, the procedure was also performed at a C/10 rate, and also increasing the charging voltage to 4.6V. Starting again with a 1mAh/cm<sup>2</sup> deposition NA anode (Figure 2.3c), the CE of the first charge/discharge cycle was 77.31% and peaking to 96.83% within the next five cycles (Figure S3b), and quickly dropping in subsequent cycles, along with the overall cell performance (Figure 2.3c). The anode had a longer cycle life and higher CE, compared at the 1C rate, where the performance of the anode died almost instantly (Figure 2.3a). The addition of 2% VC did not have as much of an effect on improving the overall cell performance, as compared to that at the 1C rate. Increasing deposition capacity to 2mAh/cm<sup>2</sup> saw a decrease in the anode's cycle life, only maintaining stable cycling for 17 cycles, compared to 44 cycles at a 1C rate. The anode with the 3mAh/cm<sup>2</sup> deposition had comparable performance to its 1C counterpart, lasting 50 cycles at the C/10 rate.

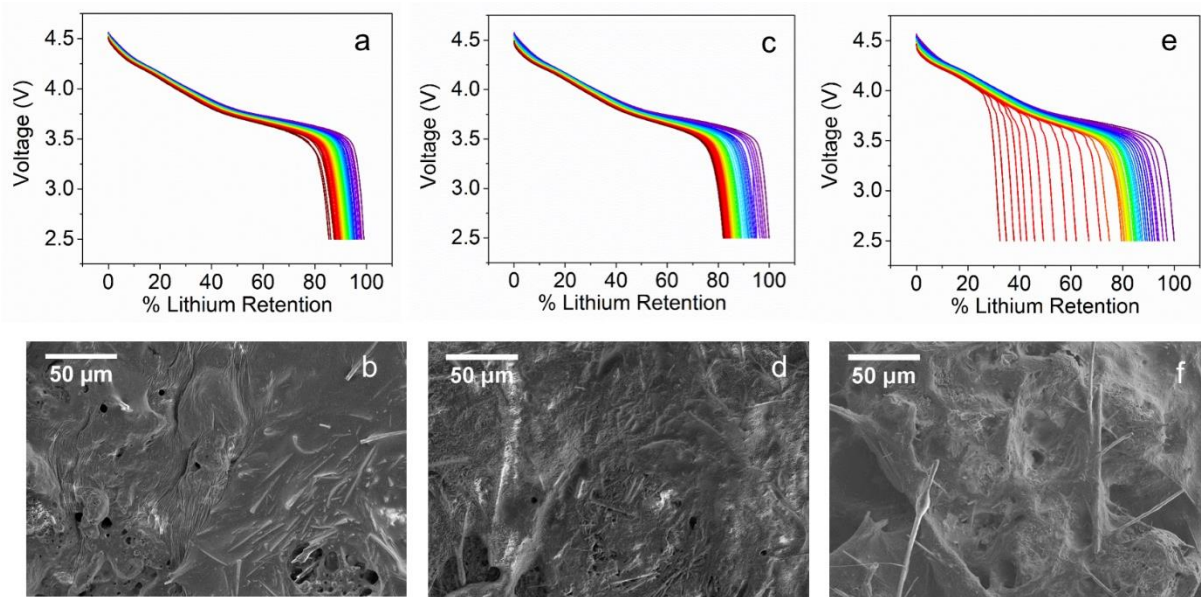


**Figure 2.4)** Full cell discharge curves and SEM images for Li/CNF surface morphology at increasing deposition rate at (a,b) 0.05 mA/cm<sup>2</sup>, (c,d) 0.5 mA/cm<sup>2</sup>, and (e,f) 1 mA/cm<sup>2</sup>.

There appears to be an initial large consumption of active lithium, either through SEI formation or other side reactions, that drastically decreases the cycle life of the anode. For cells that have less lithium loading on the anode, such as the 1 and 2mAh/cm<sup>2</sup>, this initial consumption is detrimental to the anode's lifespan. There was also an unforeseen observation with decreasing the C rate. Usually, the lower the C rate the longer anode's cycle life is due to the slow rate allowing for a more homogenous plating of lithium on the anode's surface during the charging process. The opposite trend is noticed here. It is possible that the lower C rate allows for more side reactions to occur to the traveling lithium, consuming the active lithium in an already lean anode system, allowing for faster overall active lithium depletion. Once the amount of lithium deposited passes a certain threshold, there is a noticeable increase in the cycle life of the battery as a whole seen at both C/10 and 1C rates. Most tests run by others, in comparison, include either lithium foil, or a Li/C composite with higher lithium loading, which allows others to ignore the amount of lithium consumption by having an excess amount of lithium.<sup>17,18</sup>

Another factor that affected the performance and the morphology of the anode is the rate of Li electrodeposition. Three deposition rates of 0.05mA/cm<sup>2</sup>, 0.5mA/cm<sup>2</sup>, and 1mA/cm<sup>2</sup> were chosen for the 3mAh/cm<sup>2</sup> areal capacity composite anode with 2% VC and were cycled at a C/10 rate in full cells to determine the correlation between deposition rate and performance. Figure 2.4 contains the three discharge profiles demonstrating the difference in the cycling performance and lifespan of the composite anodes. There was a pronounced deterioration in performance with an increase of deposition rate. The 1mA/cm<sup>2</sup> anode (Figure 2.4c) had a large initial capacity fade and reached the state of rapid cell failure within 30 cycles, unlike the 0.5mA/cm<sup>2</sup> and 0.05mA/cm<sup>2</sup> anodes. The initial discharge curves for 0.5 and 1mA/cm<sup>2</sup> anodes have more cycles of initial poor

capacity retention and larger gaps of fading capacity. This poorer performance seen is related to the rate of deposition. We can see that there is a difference in the homogeneity of the plated lithium on the CNF, which could be playing a role in the initial poor performance (Figures 2.4b, d and f). With the inhomogeneous morphology of the plated lithium, the SEI would not be flat, and would be unable to handle large fluctuations in the relative volume during the plating/stripping cycles of lithium. Cracks in the SEI would also occur, and expose fresh lithium to react with the electrolyte, until a stable SEI layer can form.<sup>68,69</sup> One can conclude there is a correlation between the rate of deposition and initial morphology of the composite anode and the anode's performance and cycle life.

### 2.3.4 Characterization of the SEI after electrodeposition

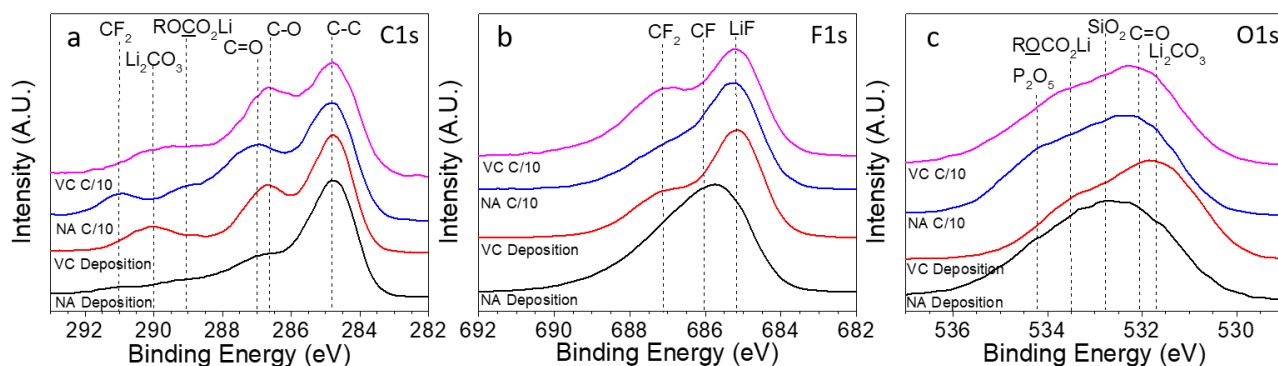


**Figure 2.5)** XPS spectra of Li/CNF composite anodes with 1mAh/cm<sup>2</sup> areal capacity after deposition and reaching a state of rapid cell failure. The anodes used an electrolyte with either no additives (NA) or 2% vinylene carbonate (VC). The **a)** C1s, **b)** F1s, and **c)** O1s chemical environments were studied to determine the SEI composition depending on the composite anode's electrochemical conditions.

XPS analysis was utilized to determine the SEI composition of the composite anodes with before and after cycling and with different electrolyte solutions. The spectra for C1s, F1s, and O1s were investigated for anodes after electrodeposition and cycling until failure at a C/10 current rate with electrolytes NA and 2% VC (Figure 2.5). Starting with C1s (Figure 2.5a) all samples maintain a strong C-C peak at 284.8 eV from the carbon fiber host material. We begin to compare the two

samples fresh from electrodeposition. A much stronger intensity for C-O (286.6 eV) and C=O (287.1 eV) containing chemical species present in sample containing VC, as would be expected knowing the decomposition and polymerization mechanism of VC.<sup>70,71</sup> The VC anode has a stronger peak intensity for Li<sub>2</sub>CO<sub>3</sub> (290.1 eV) as well. For the cycled C/10 samples, after reaching state of rapid cell failure, the SEI composition changes drastically between the NA samples. The NA C/10 anode has a strong C=O peak, and less intense peaks for RO $\overline{\text{C}}$ O<sub>2</sub>Li and CF<sub>2</sub>, while the VC C/10 sample still maintains a strong presence of C-O species, and has a stronger intensity for C=O. The intensity of Li<sub>2</sub>CO<sub>3</sub> decreased for VC C/10 compared to VC deposition as well.

The F1s spectra (Figure 2.5b), shows that LiF (685.1 eV) is present in the SEI for all samples. The NA deposition anode is the outlier, having a weaker intensity for LiF in comparison with the other anodes. The improved active lithium anode lifespan can be attributed to the stronger intensity of LiF for the VC deposition compared to NA deposition, as LiF is well known for improving Li anode performance and preventing dendrite growth.<sup>70,72,73</sup> A strong peak for CF<sub>2</sub> (687.1 eV) is seen for the VC samples, while the NA samples have a stronger presence of CF (686 eV). O1s shows large variance between the anode samples. SiO<sub>2</sub> (532.5 eV) from the glass fiber remnants embedded in the lithium metal deposition can be seen in some samples but are assumed to be not affecting anode performance. The two deposition samples showing more variation in the SEI composition, with the VC deposition anode having stronger peaks for Li<sub>2</sub>CO<sub>3</sub> (531.7 eV) and C=O (532.1 eV) for the more prominent and beneficial organic phase. After cycling at C/10 rate, the NA and VC anodes do become more similar, but NA having a stronger shoulder peak for P<sub>2</sub>O<sub>5</sub> (534.7 eV) and VC still having more prominent peaks for C=O species and Li<sub>2</sub>CO<sub>3</sub>.

The growth in the organic phase in the anodes containing VC, compared to those without, can explain the anode's improved cycle life. The enhanced organic layer from VC has been well

studied and helps improve the ionic conductivity, allowing for improved Li-ion transference to and from the anode surface and help prevent further side reactions of the electrolyte and lithium metal.<sup>22,43</sup>

### 2.3.5 Li-Graphite composite anode

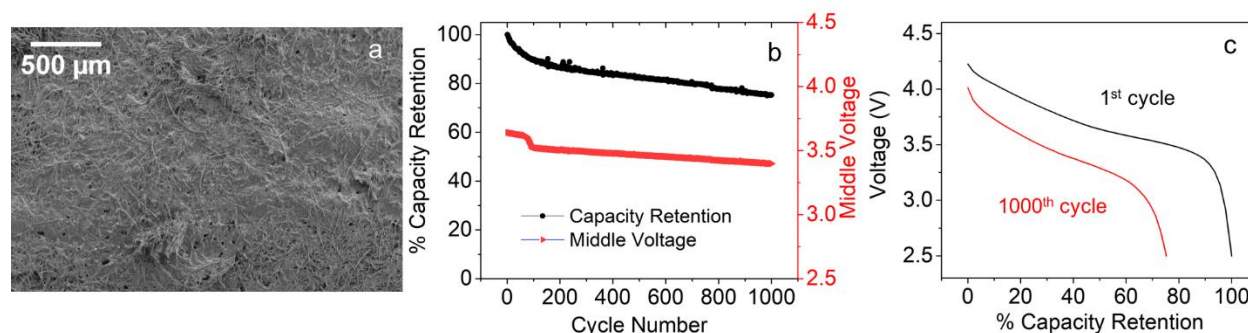


**Figure 2.6) (a)** Low-magnification SEM image for the overview of the surface morphology of Li/Graphite composite anode, **(b)** capacity retention and middle voltage profile after 1000 cycles showing stability of the anode over long cycle life, and **(c)** first and last (1000<sup>th</sup>) discharge cycle of Li/Graphite composite anode at 1C rate.

Graphite, a well-known and thoroughly researched material, was chosen to observe the effect of carbon chemical environment on the performance of the Li/C composite anode. As 3mAh/cm<sup>2</sup>, at a 1C rate with the addition of 2% VC, was shown to have the best performance for CNFs for the limited amount of lithium deposited, it was the chosen parameter to use for graphite. Low-magnification SEM shows the homogenous plating of lithium on the graphite's surface, with remnants of the glass fiber separator imbedded into the surface of the Li metal (Figure 2.6a). The initial cycling profile and CE was similar to that of the Li/CNF anode (Figure S2.8) but maintained a longer cycle life with good performance. There was rapid fade in capacity in the initial 100 cycles, which was likely attributable to the impedance growth caused by cathode failure such as surface reconstruction at high voltages.<sup>74,75</sup> After 1000 cycles, the cell retained 75% of initial capacity (Figure 2.6b), with a gradual decrease in capacity retention. Li/graphite had much better capacity

retention compared to those of the Li/CNF composites, which reached states of rapid cell failure after the active lithium was consumed. An NMC/Graphite cell was made and cycled for 1000 cycles to compare performance with our graphite composite anode. After 1000 cycles, the graphite full cell had 60% capacity retention, while our graphite composite anode maintained 75% retention. This tells us that the deposited lithium improves the performance of the cell as a whole.<sup>76</sup> The observed middle voltage also shows that the cell maintains good stability throughout the 1000 cycles, after experiencing an initial drop at the beginning, which corresponds to the initial fast capacity fade, likely due to the impedance buildup caused by the cathode fading.<sup>36</sup> The first and last discharge cycle (Figure 2.6c) show the drop in the initial discharge voltage, which is attributable to the growth of cell impedance caused by surface phase transformations on NMC particles, formation of cracks and electrolyte decomposition, decreasing performance and longevity of the cathode.<sup>74,75,77–79</sup> The improved cycle life is theorized to be due to the better long term sustainability of the graphite anode being able to lengthen the lifespan of the active lithium. These results help corroborate the high performance in other studies that report high concentration of graphitic carbon in their carbon host material.<sup>20,66,80</sup> Using SEM to observe the morphology for the initial deposition and after the 1000 cycles, we see that the lithium is plated smoothly across the surface of the graphite, and can see in some areas, that the lithium coats over, and into the layers of the graphite particles (Figure S2.9a). Cross section images show that lithium metal deposits and grows within the graphite layers. The morphology is rougher after 1000 cycles, but still has lithium metal present on the surface of the composite anode (Figure S2.9b).

The performance of the graphite composite anode suggests that the inclusion of graphitic carbon could be a key factor to increasing the longevity and protecting the active lithium to ensure longer cycle life. Future research would need to more thoroughly investigate the importance

between the Li-C bonds that can improve and sustain lithium longevity and increase the lifespan of composite anodes with carbonaceous host materials.

## 2.4 Conclusion

Previous studies of lithium metal anodes have primarily utilized bulk lithium metal (e.g., lithium foil), which could not represent practical lithium metal batteries where the loading of lithium metal must be minimized for improving safety and energy density. In this work, the formation of the Li/CNF composite anode has allowed us to design a lithium-limited full cell system, which has not been a heavily investigated area of research. The major benefit of using the electrodeposition method for inserting lithium is that the limited system allowed us a fast turnaround with observing changes in cell performance and cycle life based on modifications to the anode, either in total deposition capacity of lithium, or rate of electrodeposition, the electrolyte system, with the addition of electrolyte additives, and the change in C rate. We have found that the rate of consumption of composite anodes with mass loading to bypass the large initial consumption of lithium has a lifespan of ~23 cycles (1C rate) per mAh/cm<sup>2</sup>. The increase in rate of deposition was found to have a negative effect on the cycling life of the composite anode due to the inhomogeneous plating of lithium on the CNF with increasing rate. XPS has shown that the addition of VC has increased the organic phase and the LiF content, while decreasing Li<sub>2</sub>CO<sub>3</sub> to account for the increase in cell cycle life. Lastly, the deposition of lithium into a graphite anode has shown that graphite can lengthen the lifespan of active lithium and giving good cycle performance, with a capacity retention of 75% after 1000 cycles. Graphitic carbon has an influential effect on increasing the longevity of active lithium in the composite anode and requires further investigation to determine the importance of the Li-C bonding environment to improve the lifespan of lithium. Finally, our study calls for utilizing limited lithium loading for investigating

the anode chemistry in lithium metal batteries in order to remain relevant to future practical applications.

## 2.5 Experimental Section

### 2.5.1 Materials Synthesis

Walnut shell (*Juglans Sigillata*) was ground ( $>100$  mesh) and dried in an oven at  $80\text{ }^{\circ}\text{C}$  before use. The mixture of walnut shell powder, phenol, and sulfuric acid (concentrated 98%) at a mass ratio of 1:4:0.03 was liquefied for 2 hours at  $150\text{ }^{\circ}\text{C}$ . Subsequently, the mixture was poured into dioxane/water (8/2, v/v) at a volume ratio of 1/15. The diluted solution was filtrated and concentrated under reduced pressure to obtained impurities-free liquefied products. The liquefied phenol formaldehyde resin (LPF) was synthesized by formaldehyde (F), liquefied products (LP) with sodium hydroxide (NaOH) as catalyst (molar ratio,  $\text{F/LP} = 1.45/1$ ,  $\text{NaOH/LP} = 0.2/1$ ). In synthesizing resin (LPF), LP, NaOH solution and 80 % of the total F were added into a three-neck flask. The solution was heated to  $82\text{ }^{\circ}\text{C}$  for 60 min. After that, the remaining 20 % of F was added. Reaction temperature was increased to  $87\text{ }^{\circ}\text{C}$  and kept for 120 min under stirring, followed by cooling to room temperature. Subsequently, the synthesized LPF was diluted to 18 wt% in solid content with distilled water and 12 wt% polyvinyl alcohol (PVA) aqueous solution added into the LPF to adjust the electrospinnability (mass ratio of  $\text{LPF/PVA} = 8/2$ ). The mixed solution stirring was continued for 2 h. Electrospun nanofibers were prepared by electrospinning device (ET-2535H, Ucalery), which consisted of a high voltage power supply, a syringe pump, and a roller (covered with an aluminum foil) connected to the negative pole for collecting the fibers. The spinning solution was loaded into a 5 mL plastic syringe with a 22-gauge needle connected to the positive pole of a voltage generator. During spinning, the distance was adjusted to 25 cm between the tip

of needle and the roller, an operating voltage was ranged from 16 kV and the feeding rates of spin was maintained at 0.05 mL/min. The carbon nanofibers were fabricated by one-step carbonation at 900 °C at a rate of 5 °C/min and held for 60 min in a nitrogen atmosphere.

$\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  was synthesized using a co-precipitation method with  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (Sigma Aldrich, 99.99%),  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (Sigma Aldrich, 99%) and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma Aldrich, 99%) as the raw materials. The transition metal solution (0.06 M  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , 0.02 M  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and 0.02 M  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in 100 mL  $\text{H}_2\text{O}$ ), starting solution (40mL NaOH and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  aqueous solution with a molar ratio  $\text{NaOH}/\text{NH}_3 = 1.2$ , pH value was adjusted to 10.5) and base solution (100 mL NaOH and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  aqueous solution with a molar ratio  $\text{NaOH}/\text{NH}_3 = 1.2$ ) were made and separately stored in Kimble bottles. The transition metal solution and base solution were simultaneously pumped into the starting solution at a drop rate of  $\sim 2$  mL/min with continuously stirring at 50 °C under the  $\text{N}_2$  protection. The drop rate of the base solution was frequently tuned to keep the pH at  $10.5 \pm 0.2$ . The precipitate was collected, washed, and filtrated with DI water and dried in vacuum oven overnight at 100 °C. The dried precursor was then mixed with LiOH thoroughly and calcined under air flow (2 L/min) at 725 °C for 6 hours to obtain the final  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  powder.

### 2.5.2 Materials Characterization

The morphologies of the materials were investigated using a scanning electron microscope (SEM) (LEO FESEM) at the accelerated voltage of 5 KV. FTIR spectra were collected using PerkinElmer Spectrum One FTIR in the wavenumber range of 700-1800  $\text{cm}^{-1}$ . Raman spectra were collected using a PerkinElmer Raman-Station 400. XPS characterization was performed on a PHI VersaProbe III scanning XPS microscope using monochromatic Al K-alpha X-ray source (1486.6 eV). Samples were transferred from an Ar-filled glove box to the XPS ultra-high vacuum chamber

via a vacuum transfer vessel. XPS Spectra were acquired at 10  $\mu\text{m}/100\text{ W}/20\text{ kV}$  over  $1400\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$  sample area using 26 eV pass energy, which gives a  $\text{Ag}3d_{5/2}$  full width at half maximum of 0.59 eV. All binding energies were referenced to C-C peak at 284.8 eV.

### 2.5.3 Electrode Preparation and Electrochemical Testing

The graphite electrode was prepared using CGP-C8 graphite powder (Conoco Phillips, 90 wt.%) and PVdF (10 wt.%) which were mixed into a slurry (N-Methyl-2-pyrrolidone as the solvent) and spread onto copper foil. The electrodes were dried overnight at  $100^\circ\text{C}$  in a vacuum oven and transferred into an Ar filled glovebox for future use. The lithium metal electrodeposition uses the electrolyte 1M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) dissolved in ethylene carbonate/ethyl methyl carbonate (EC/EMC, 3:7, by weight, BASF) with or without additives. The additives used in this study include 2%, by weight, vinylene carbonate (VC, Sigma Aldrich 97%) and 2%, by weight, fluoroethylene carbonate (FEC, Alfa Aesar 98%). The composition of the coin cell (CR 2032 model) for electrodeposition consisted of the carbon nanofiber disc ( $2\text{ cm}^2$ ) placed onto a copper foil current collector ( $2\text{ cm}^2$ ), or a graphite electrode, as the positive electrode with a disc of Li foil as the negative electrode, with a glass fiber separator. The electrodeposition of lithium was performed using a Maccor Model 4200 series battery testing equipment. The electrodeposition process was set between  $1\text{-}3\text{mAh}/\text{cm}^2$  total areal capacities using deposition rates between  $0.05\text{-}1\text{mA}/\text{cm}^2$ . After the deposition of lithium into the CNF matrix or graphite electrode, the coin cell was deprimed to retrieve the lithiated CNF or graphite composite anode. The composite cathodes (with active mass loading of  $\sim 3.5\text{ mg}/\text{cm}^2$ ) were prepared by spreading the slurry (N-Methyl-2-pyrrolidone as the solvent) with active  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  materials (90 wt.%), acetylene carbon (5 wt.%) and PVdF (5 wt.%) as the binder and casting them on carbon-coated aluminum foils. The electrodes were then dried overnight at  $120^\circ\text{C}$  in a vacuum oven and transferred into an Ar filled

glove box for future use. To test the performance of the Li/C composite anodes were combined with  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC622) cathodes with glass fiber separators and 1M  $\text{LiPF}_6$  EC/EMC electrolyte (with 2% VC by weight). The full cells were cycled using Land battery testing systems. In cycling full cells, 1C was defined as fully charging a cathode in 1 h, corresponding to a specific current density of 200 mA/g.

## 2.6 Acknowledgement

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## 2.7 Supporting Information

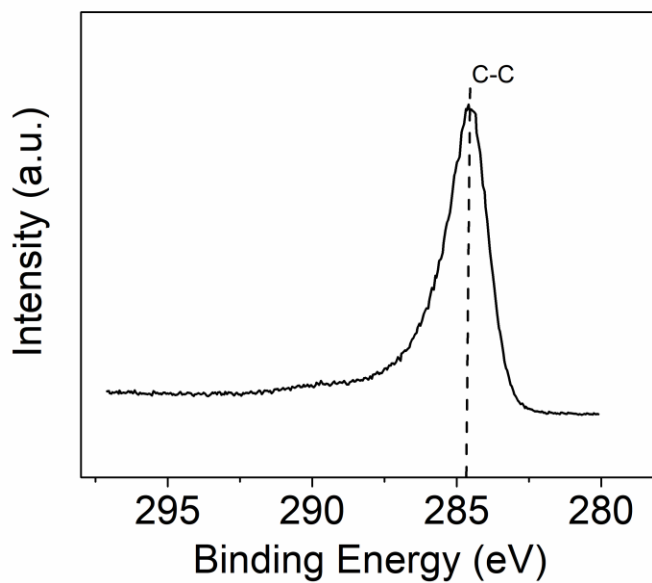


**Figure S2.1)** C1s XPS for pristine CNF showing the surface functionalization consists mostly of the C-C bond (284.8 eV).

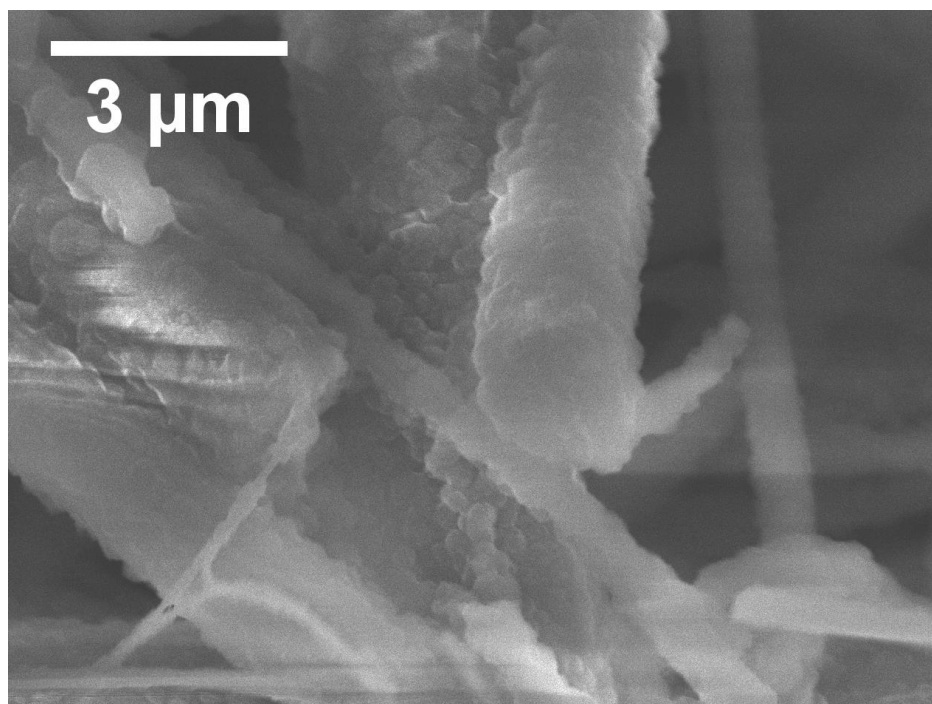


**Figure S2.2)** High resolution SEM image of Li/CNF after 1mAh/cm<sup>2</sup> of Li electrodeposition at 0.05mA/cm<sup>2</sup> deposition rate showing the coating of Li on the CNF, changing the morphology from the smooth surface of the pristine CNF to one that is rigid and coated with Li metal.

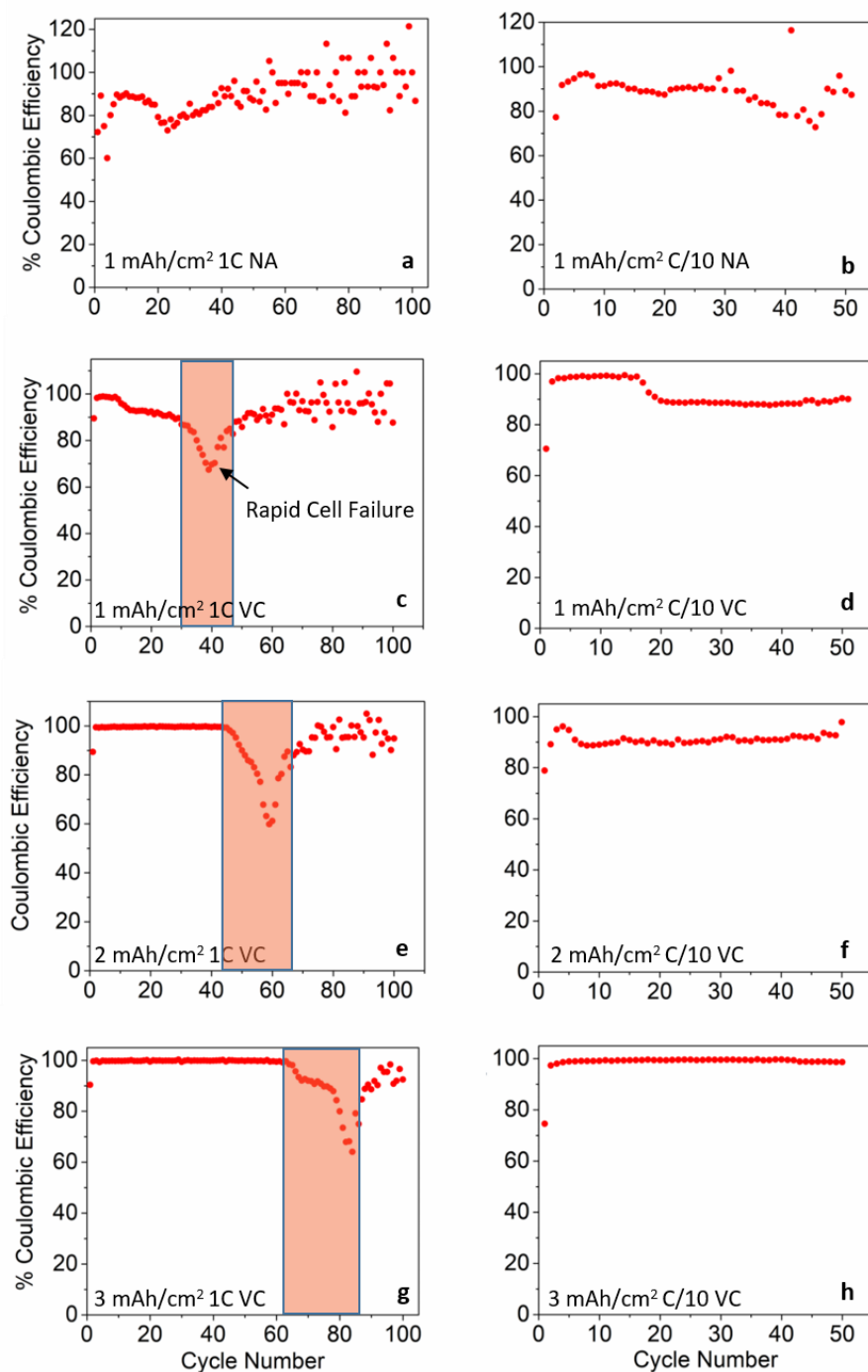


**Figure S2.3)** Coulombic efficiencies for Li/CNF composite anodes with varying total areal capacities and cycled current rates 1mAh/cm<sup>2</sup> with no electrolyte additive cycled at 1C (**a**) and C/10 (**b**), 1mAh/cm<sup>2</sup> with VC (2 wt.%) at 1C (**c**) the rapid cell failure in which the active lithium is consumed is highlighted in the decline in the Coulombic efficiency, and C/10 rate (**d**), 2 mAh/cm<sup>2</sup> with VC at 1C rate (**e**) and C/10 rate (**f**), and 3 mAh/cm<sup>2</sup> at 1C (**g**) and C/10 (**h**)

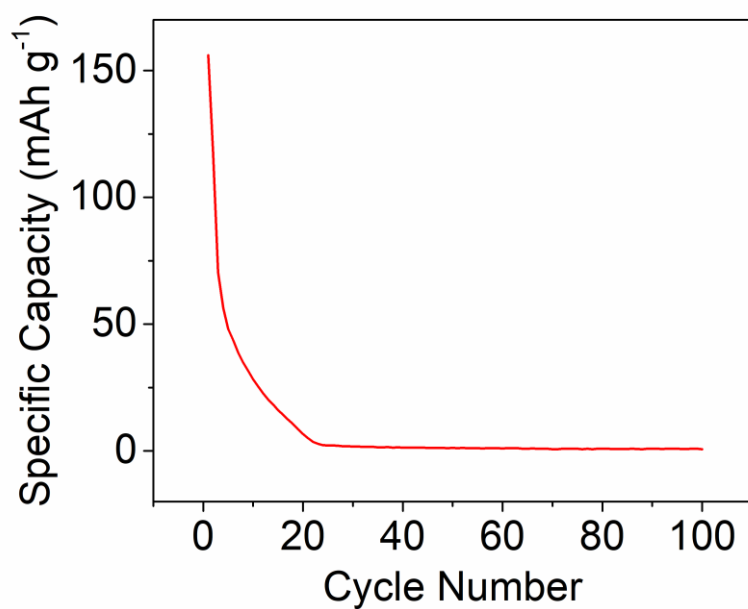


**Figure S2.4)** Specific capacity v cycle number for Li/CNF composite with a deposition of 1mAh/cm<sup>2</sup> with no electrolyte additives.

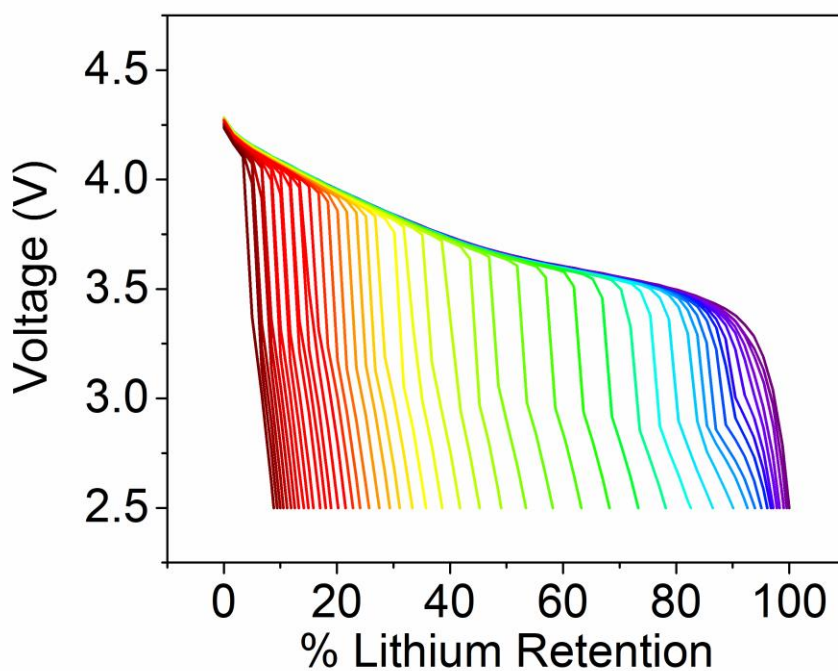


**Figure S2.5)** Lithium retention discharge curves for 1 mAh/cm<sup>2</sup> with the addition of 2% VC Li/CNF composite with 622 NMC cathode, showing the formation of the “knees” that indicate the beginning of rapid loss of active lithium in the composite anode.

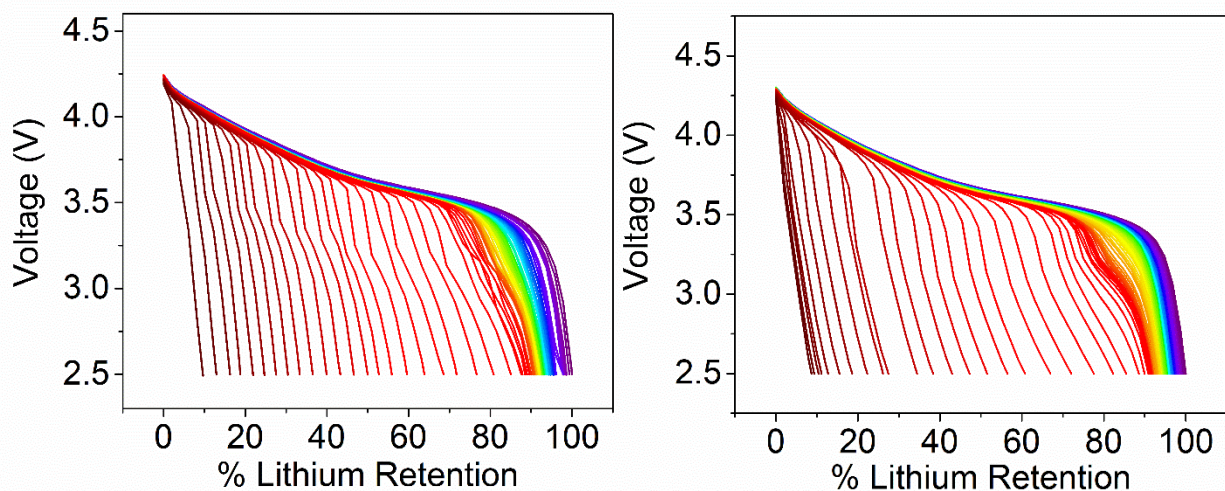


**Figure S2.6)** Lithium retention discharge curves for replicated full cells for  $3\text{mAh}/\text{cm}^2$  Li/CNF composite with 622 NMC cathode.

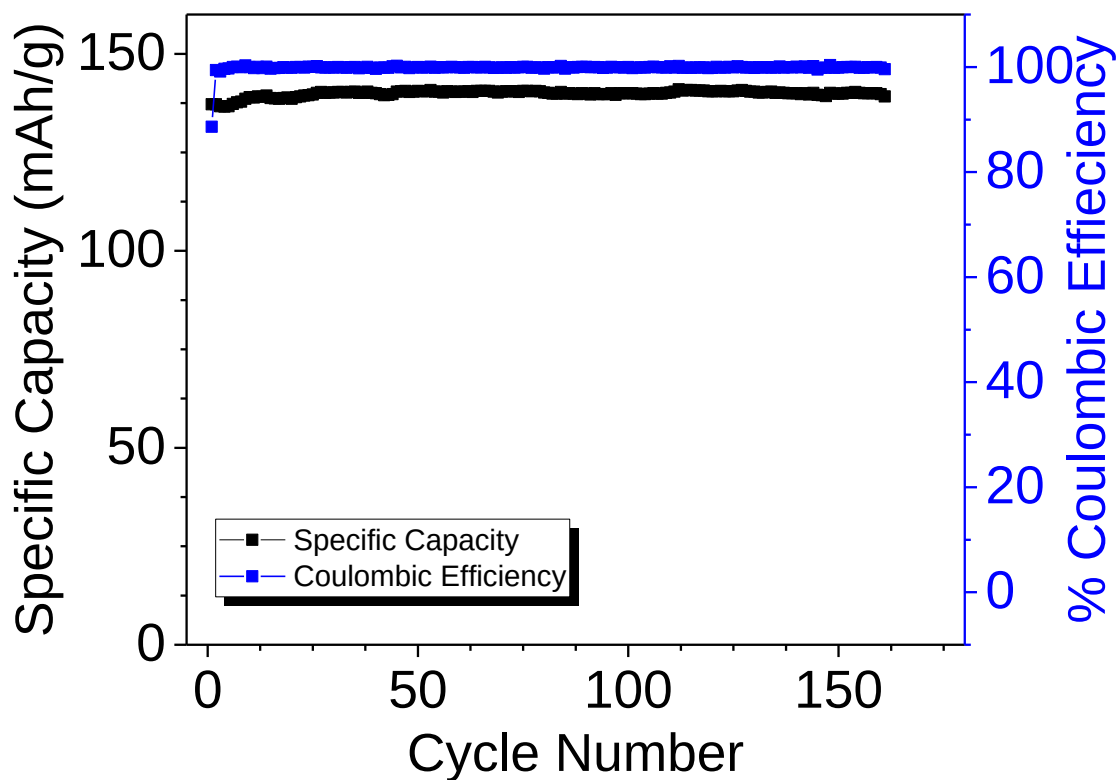


**Figure S2.7)** Specific capacity and CE of a retrieved cathode from a composite anode cell, after reaching a state of rapid cell failure. The cathode was used in a new cell with a fresh lithium metal anode and cycled to determine that the capacity fade in the CNF composite anode was not primarily due to the cathode.

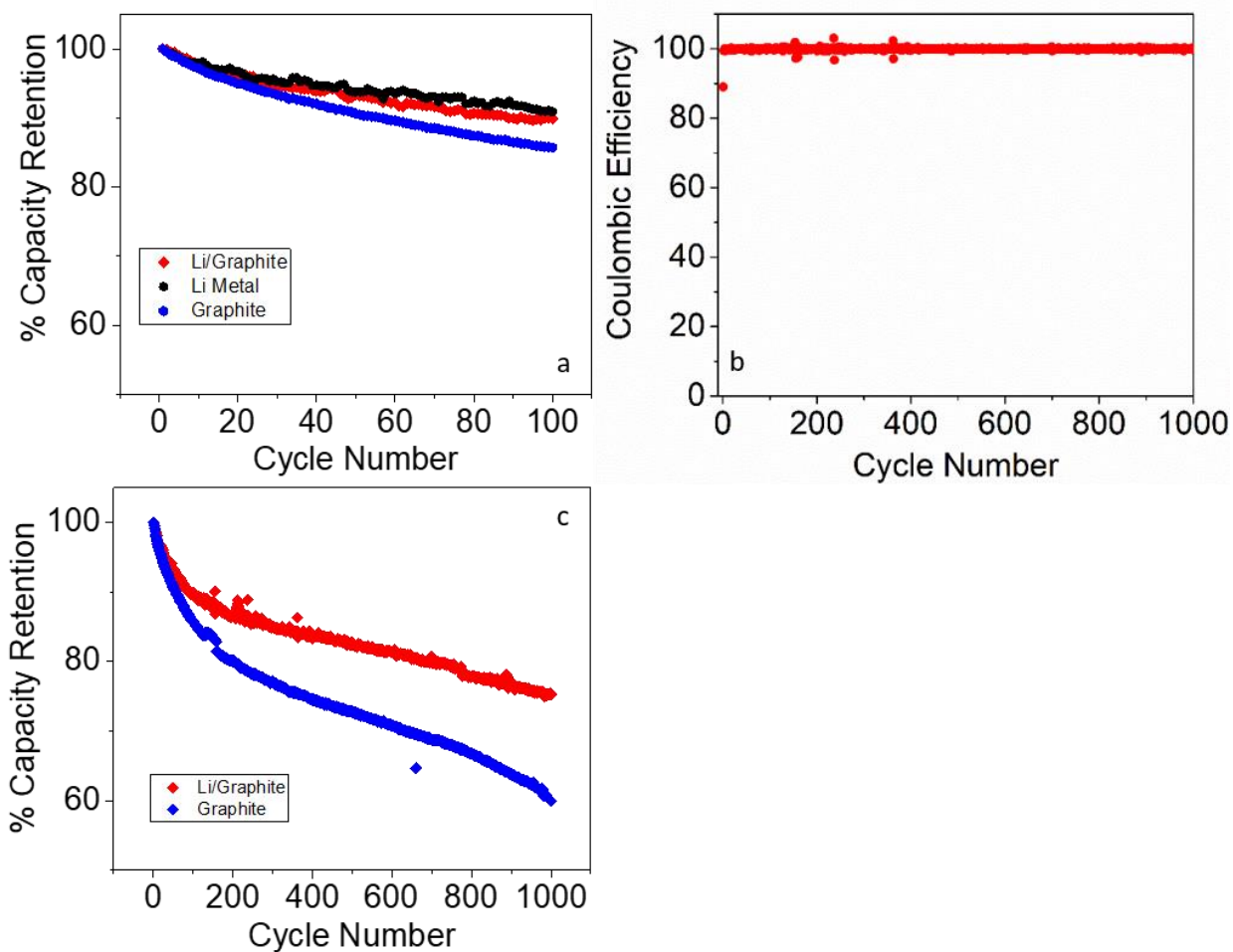


**Figure S2.8) (a)** Specific capacity retention for the first 100 cycles comparing Li/Graphite composite anode against lithium metal and bare graphite anodes **(b)** Coulombic efficiency for Li/Graphite anode over 1000 cycles **(c)** specific capacity retention for 1000 cycles comparing Li/Graphite composite anode to bare graphite anode. All full cells utilize 622 NMC cathode.

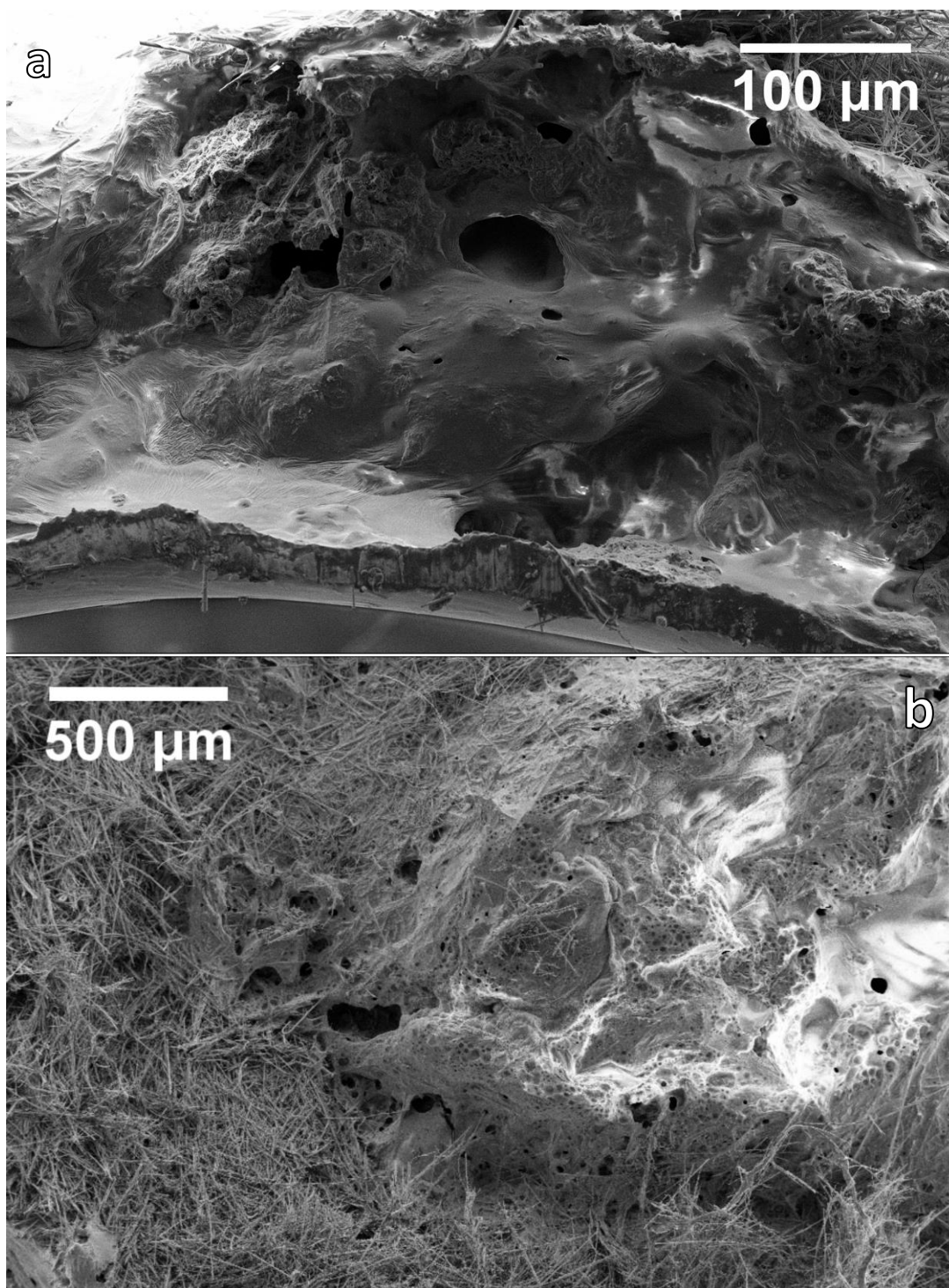


**Figure S2.9)** SEM images for **(a)** Cross section of Li/graphite composite electrode after electrodeposition highlighting that lithium does deposit throughout and coats through the graphite particles and **(b)** surface morphology of Li/graphite composite electrode after 1000 cycles. Lithium metal is still present, but the surface morphology has changed to an overall rougher and more porous morphology.

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### 3. Investigating “Lean” Electrodeposited Lithium and Sodium Metal for Hybrid Ion/Metal Carbon Composite Anodes

*David J. Kautz, Lei Tao, Linqin Mu, Muhammad Mominur Rahman, Chunguang Kuai, Zhifeng Zheng, and Feng Lin \**

#### 3.1 Abstract

The implementation of alkali metal anodes in practical batteries have been unsuccessful due to major safety concerns related to dendritic growth and thermal runaway. Carbon scaffolds have been utilized as promising host materials in an effort to improve battery safety and performance. Herein, “lean” lithium and sodium composite anodes, using a semi-crystalline carbon nanofiber (CNF) host material with limited surface functionalization, are utilized to investigate the relationship between the structural characteristics of the CNF and lithium/sodium metal. Symmetric testing reveals that the Na-CNF composite anode maintains stable cycling performance, with minimal hysteresis increase over 2000 hours, whereas Li-CNF fails before 200 hours. When paired with layered oxide cathodes ( $\text{NaNi}_{0.33}\text{Fe}_{0.3}\text{Mn}_{0.33}\text{Ti}_{0.04}\text{O}_2$  and  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  for sodium and lithium cells, respectively) and cycled at 1C, the Na-CNF cells maintain 75% capacity retention after 500 cycles, but the Li-CNF cells fail shortly after 140 cycles. The primary factor enabling stable long-term cycling for Na-CNF cells is that Na ion undergoes reversible ion intercalation, whereas Li ion is limited to surface adsorption. The inherent carbon crystallinity is found to govern the interaction between the carbon host and alkali metals and is a primary factor in the sustainability and performance of the metal composite anodes.

## 3.2 Introduction

Batteries with higher energy density are pivotal to support the rapid development of technologies, such as electric vehicles and portable electronics. Conventional graphite anodes will be unable to meet these energy demands with its low theoretical capacity ( $372 \text{ mAh g}^{-1}$ ).<sup>1</sup> The reliance on graphite as the commercial anode of choice is unsustainable and will hinder technological innovation due to graphite's impractical volumetric requirements. Throughout the past several decades there has been a determined effort to enable lithium metal as an alternative anode material for secondary batteries due to its high theoretical capacity ( $3860 \text{ mAh g}^{-1}$ ), low density ( $0.534 \text{ g cm}^{-3}$ ), and low redox potential ( $-3.040 \text{ V}$  vs Standard Hydrogen Electrode, SHE). Lithium metal anode has been utilized in various designs for next-generation batteries such as Li-nickel rich layered oxides, Li-S, and Li-O<sub>2</sub>.<sup>2-5</sup> However, lithium metal anodes face many challenges stemming from its high reactivity with electrolyte, unstable solid electrolyte interphase (SEI) formation, and dendrite formation, which collectively results in poor Coulombic efficiency (CE), high hysteresis, and severe safety risks. Various strategies have been employed to improve lithium metal anode performance and reduce safety concerns, including the utilization of electrolyte additives<sup>6-8</sup>, artificial SEI<sup>9,10</sup>, and surface modifications.<sup>11-13</sup> More recently, utilizing 3D carbon scaffold current collectors to form metal composite anodes has been a major research effort to contain lithium metal expansion, homogenize local charge density, and limit the lithium metal loading (i.e., “lean” anode).<sup>1,14,15</sup> To develop a practically viable lithium metal anode, a “lean” composite anode ( $<5 \text{ mAh cm}^{-2}$ ) should be able to sustain long-term cycling and prevent consumption of the limited active material.<sup>1</sup> Multiple previous reports have utilized doping<sup>16,17</sup>, surface functionalization<sup>18-20</sup>, and structural modification<sup>21</sup> of the carbon host to improve the host-guest interaction to increase the lifespan and cycling performance of composite anodes. Although

limiting the use of Li metal is critical for practical cells, the “lean” composite anode has been overlooked compared to the composite anodes that use an excess amount of lithium metal.<sup>[17,20,21]</sup>

As a potential alternative anode material, sodium metal anode has more recently become a prominent point of interest for secondary battery applications. Sodium metal has a moderately high theoretical capacity (1166 mAh g<sup>-1</sup>), low redox potential (-2.71 V vs SHE), and moderately low density (0.971 g cm<sup>-3</sup>). The natural abundance of sodium in the Earth’s crust is orders of magnitude higher than that of lithium, making sodium batteries potentially more cost-effective than lithium. Sodium batteries are mostly attractive for large scale energy grid applications, where size and portability are not the major deciding factors for utilization. However, sodium metal faces many of the same problems that surround lithium metal anodes, such as poor Coulombic efficiency and dendrite formation. Sodium also faces another unique issue. Unlike other alkali metals, sodium has unfavorable interactions with carbon materials.<sup>25,26</sup> Sodium ions are generally unable to intercalate into graphite as easily as lithium ions. For sodium ions to intercalate into graphite, a large overpotential is required to overcome the energy barriers necessary for ion intercalation, removing graphite as a viable anode material for sodium ion batteries.<sup>26–28</sup> Hard carbon has been the primary anode material for sodium ion batteries due to the larger (002) d-spacing (3.6–3.9 Å), and Na ions adsorbing onto the surface defects and nanovoids present in hard carbon.<sup>29–31</sup> Multiple studies have reported and debated about the adsorption-insertion mechanism of Na ions in the hard carbon electrode.<sup>29,31–34</sup> Sodium metal composite anodes have also begun to be more heavily investigated recently.<sup>35–37</sup> With the inherent differences in how lithium and sodium interact with carbon materials, it is imperative to ascertain the critical host-guest interactions to improve the synergy, sustainability, and performance of the composite anodes. There have not been many studies on the direct comparison between lithium and sodium metal or on establishing the

relationship between the host material, electrochemical characteristics, stability, and performance. However, understanding the key factors that influence the chemical interaction between alkali metals and a carbon host will inform better design of “lean” composite anodes.

Herein, we present a thorough comparison study between lithium and sodium metal composite anodes, under “lean” ( $3 \text{ mAh cm}^{-2}$ ) conditions, using a semi-crystalline CNF membrane as the host material. We observe major differences between lithium and sodium in terms of the electrodeposition behavior, morphology, and cycling performance. Through kinetic analysis, we determine that the primary ion interaction mechanisms between Na ions and the CNF host are intercalation and adsorption, while Li ions are primarily limited to surface adsorption on the CNF host. When assembled in the full cells, containing layered cathodes, the Na-CNF composite anode can sustain much longer cycle life than the Li-CNF composite anode. The enhanced interaction between Na ions and the crystalline domain of the CNF is shown to be the determining factor for the longevity and sustainability of the sodium composite anode. The crystallinity of the host material is an important factor in the overall performance of the composite anode. Therefore, beyond controlling the surface chemistry of carbon host materials<sup>17,18,23</sup>, future work on “lean” composite anodes should also focus on optimizing the host crystallinity for lithium and sodium metal, individually.

## 3.3 Results and Discussion

### 3.3.1 Characterization of pristine carbon nanofiber

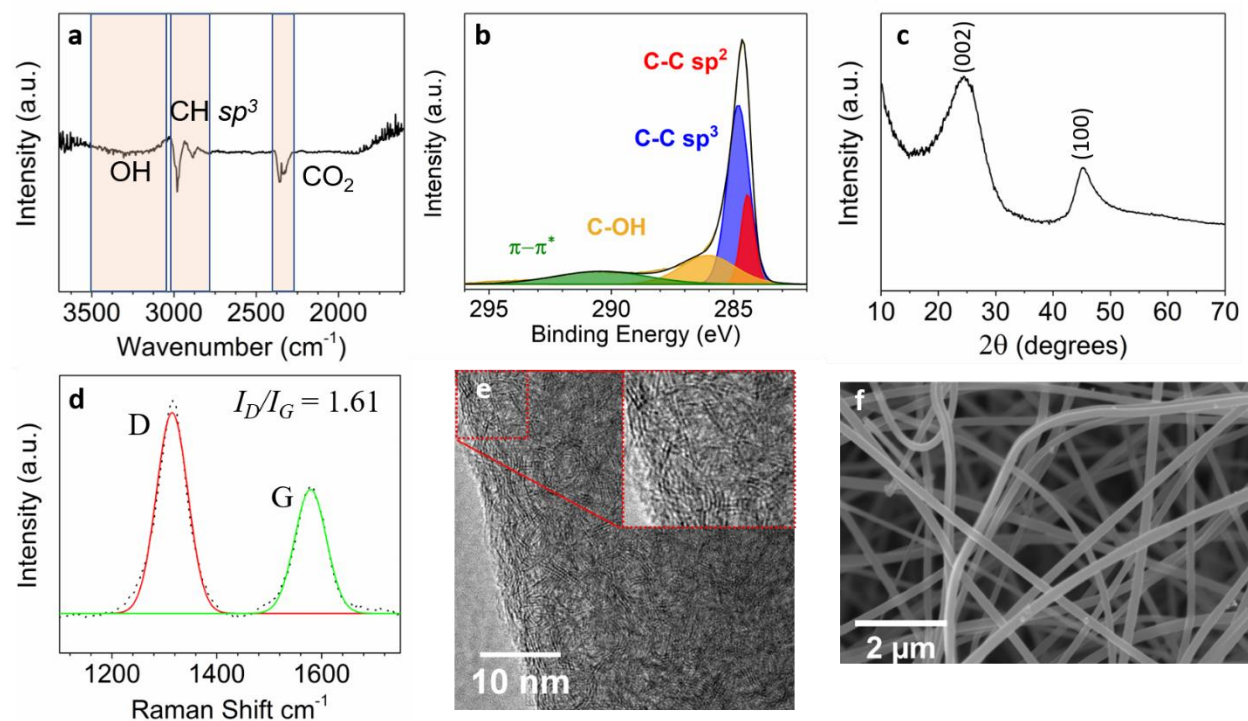


**Figure 3.1)** Characterization of the pristine CNF membrane. Surface functionalization analysis of the CNF using **a)** FTIR spectrum and **b)** Deconvoluted XPS C 1s spectra illustrating the limited presence of oxygen related surface functional groups on the CNF. **c)** XRD pattern and **d)** Raman spectra delineating the physical properties and degree of inherent crystallinity throughout the CNF membrane. Representative **e)** TEM image with the inset showing the local crystalline domains and **f)** high magnification SEM image of the pristine CNF membrane.

In-depth characterization analysis was performed to determine the surface functionalization, degree of crystallinity, and structural properties of the CNF host membrane (Figure 3.1). Through the determination of the CNF properties, we will be able to better understand the chemical interaction between alkali metals and the CNF host. Fourier transformed infrared spectroscopy (FTIR) showed minimal surface functionalization on the CNF membrane, with a weak -OH band and adsorbed CO<sub>2</sub> to the surface of the CNF (Figure 3.1a). C 1s X-ray photoelectron spectroscopy (XPS), confirmed the limited presence of oxygenated species. The sp<sup>2</sup> C-C (284.2 eV) and

crystalline  $\pi$ - $\pi^*$  satellite peaks observed ( $\sim 291$  eV)<sup>37,38</sup>, establishes the presence of ordered crystalline layers of the CNF (Figure 3.1b). The O 1s further confirmed that -OH is the only oxygen containing functional group present on the surface of the CNF (Figure S3.1) and compositional analysis from the XPS analysis shows that the CNF contains 97.6% C and 2.4% O (H is not probed). Through X-ray diffraction (XRD), two broad peaks at (002) and (100) are observed (Figure 3.1c). The  $d_{002}$  peak at  $24.8^\circ$  corresponds to the diffraction of a graphitic crystalline lattice with a calculated d-spacing of 3.59 Å using the Bragg's law, which is within the range between hard carbon materials and pure graphite  $d_{002}$  at 3.35 Å.<sup>29,39</sup> The degree of crystallinity was determined through Raman spectroscopy (Figure 3.1d). The two narrow peaks with a clear separation between the D band (1200-1500  $\text{cm}^{-1}$ ) and the G band (1500-1700  $\text{cm}^{-1}$ ), reveal the presence of well-developed hexagonal carbon structures in the CNF.<sup>40</sup> The peak area  $I_D/I_G$  ratio is 1.61, indicating a mostly amorphous material with some degree of crystallinity. Through transmission electron microscopy (TEM), the crystalline layers are observed to be, on average, 3-5 layers thick with a pattern of turbostratic crystalline ribbons that thread throughout the CNF structure (Figure 3.1e). The surface of the CNF to be generally smooth through scanning electron microscopy (SEM) imaging (Figure 3.1f). The Brunauer–Emmett–Teller specific surface area was calculated, utilizing the N<sub>2</sub> gas adsorption/desorption isotherms, to be 18.8  $\text{m}^2 \text{g}^{-1}$  (Figure S3.2). From the structural information gathered through these characterization analyses, the CNF can be described to have a semi-crystalline composition and structure. The determination of the inherent crystallinity and surface functionalization will give insight into understanding the electrochemical behavior of Li/Na-CNF composite anodes.

### 3.3.2 Electrodeposition characterization for Li/Na composite anodes

The surface functionalization and graphitization content determine the lithio/sodiophilicity of the substrate and the deposition characteristics of lithium and sodium metal.<sup>18,41</sup> Through the utilization of electrodeposition, the morphology of the electrodeposited lithium and sodium metal as well as the interaction between lithium/sodium and the CNF host is investigated. We use a metal deposition of  $3 \text{ mAh cm}^{-2}$  areal capacity (lithium or sodium metal) to test the feasibility of utilizing a “lean” anode for practical cycling conditions.<sup>1</sup> The deposition profiles presented for the metal-carbon nanofiber composites (M-CNF) are an average of three separate electrodepositions, with red error bars included (Figure 3.2a,d). In the Li-CNF electrodeposition profile, the voltage immediately drops to below 0 V, beginning the nucleation of the lithium metal phase, with a nucleation overpotential of 17 mV (Figure 3.2a). Despite the CNF having crystalline domains, there is no direct observation of the voltage plateaus indicative of the  $\text{LiC}_y$  formation during electrodeposition, that is typically observed  $\sim 0 - 0.2 \text{ V}$  (Figure 3.2a).<sup>27,42,43</sup> However, when performing electrodeposition of lithium metal on graphite, the prominent voltage plateaus of  $\text{LiC}_y$  and  $\text{LiC}_6$  are observed (Figure S3.3a). Lithium metal nucleation and plating is shown to occur earlier on the CNF substrate, compared to graphite. The quick drop in voltage to 0 V and lack of distinctive intercalation plateaus for Li-CNF (Figure 3.2a) implies that the semi-crystalline CNF does not readily undergo Li ion intercalation, unlike graphite. The Li nucleation potential on graphite is 5 mV, which is smaller than that observed for the CNF (17 mV) (Figure S3.3a). The crystalline domains in graphite are much more ordered than those in the CNF, which allows for enhanced electron transfer kinetics and overlap of the alkali metal ion and the  $\pi$  bonds between graphitic layers.<sup>27</sup>

The Na electrodeposition on the CNF shows a prominent distinction in the deposition behavior (Figure 3.2d). Two small bumps are observed at 0.38 V and 0.33 V due to initial side reactions, decomposition of the electrolyte, and SEI formation.<sup>29,39,44</sup> Similar to the Li-graphite profile (Figure S3.3a), the nucleation peak is observed further into the electrodeposition process, occurring at 1.25 mAh cm<sup>-2</sup>, with a nucleation overpotential of 5 mV. The sloping region before the Na metal nucleation can be attributed to the Na ion adsorption into the defect sites or nanovoids present in the CNF.<sup>32,39</sup> The different electrodeposition profiles may signify the contrasting interaction that the Li and Na have with the CNF host.

After electrodeposition, XRD was utilized to investigate the occurrence of lithium or sodium ion intercalation into the CNF. Although a prominent intercalation plateau is not observed for the Li electrodeposition on the CNF, a peak shift from 24.8° to 20.0° is observed in the XRD pattern. A  $d_{002}$  expansion of 0.85 Å is calculated, slightly larger than the Li<sup>+</sup> ionic radius of 0.76 Å, indicating the occurrence of Li ion intercalation. For the Na electrodeposition on the CNF, a larger peak shift to 18.6° is observed at both 0.35 V and 0 V (Figure 3.2), correlating to a  $d_{002}$  expansion of 1.18 Å, similar to the Na<sup>+</sup> ionic radius of 1.02 Å.<sup>27,45</sup>

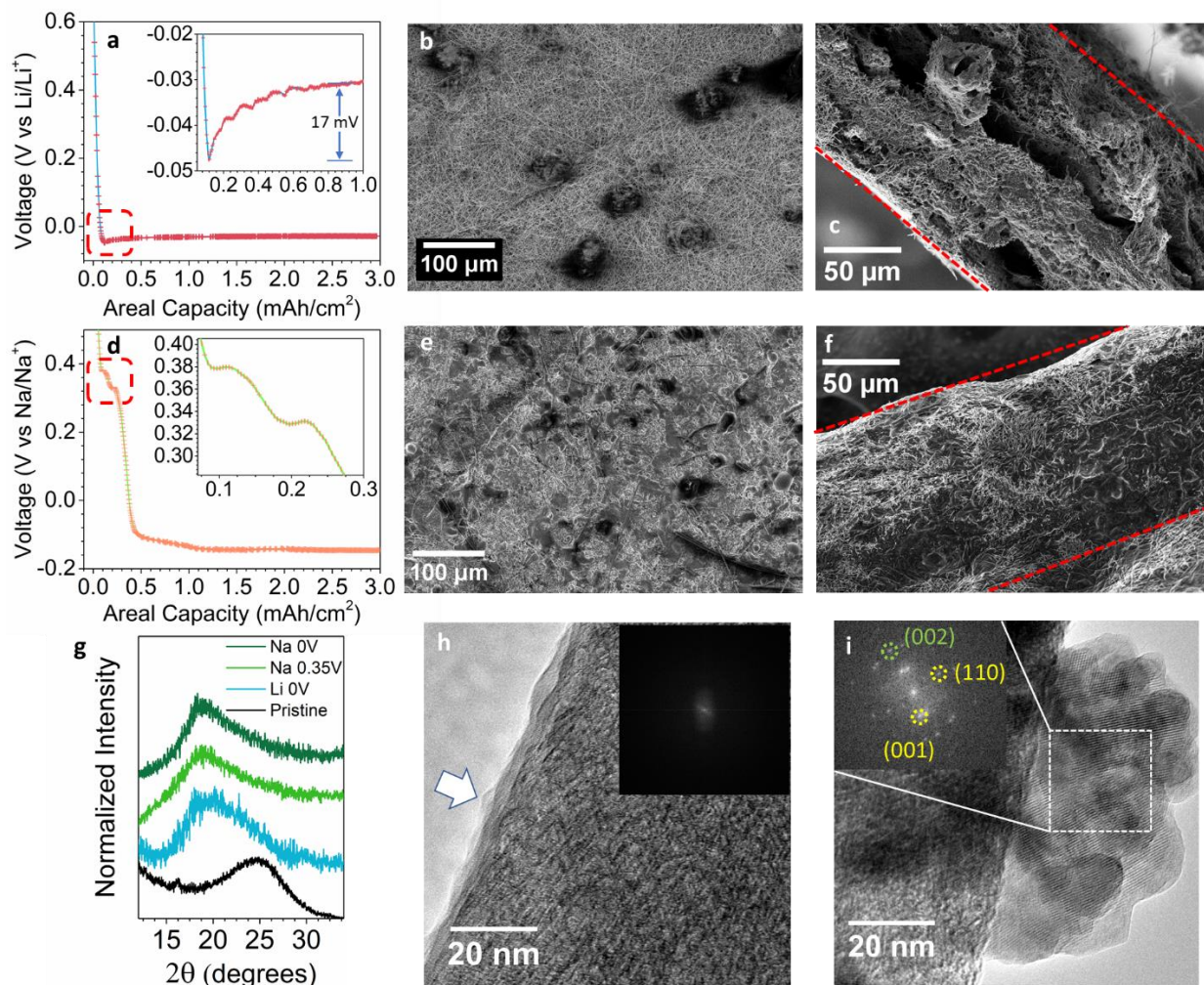


**Figure 3.2)** **a)** Li electrodeposition profile on the fresh CNF host (Li-CNF). **b,c)** SEM images of the top side and cross section of Li-CNF. **d)** Na electrodeposition profile on the fresh CNF host (Li-CNF) **e,f)** SEM images of the top side and cross section of Na-CNF. **g)** XRD pattern of the pristine CNF and after discharging to different voltages. TEM images of **h)** Li-CNF and **i)** Na-CNF after 3 mAh cm<sup>-2</sup> metal deposition with inserts of FFT dot patterns of the surface compounds on the electrodes. The deposition profiles presented for the M-CNFs are an average of three separate electrodepositions, with red error bars included in **a** and **d**.

SEM was taken for the composite anodes after electrodeposition to examine Li/Na metal plating behavior. The Li-CNF composite anode was found to have heterogenous plating of lithium metal scattered throughout the surface on the topside of the CNF (Figure 3.2b). Lithium metal preferred to gather in large clusters and did not envelope the CNF as a coating layer. With the high carbon and low oxygen content and lack of surface functionalization, the CNF host was found to be lithiophobic and did not undergo homogenous lithium plating throughout the electrode.<sup>18</sup> The

bottom side of the electrode was also inspected to view the penetration of Li metal throughout the CNF membrane. Smaller lithium metal clusters were heterogeneously plated along the bottom of the CNF (Figure S3.4a,b). Metal clusters were observed in the cross section as well (Figure 3.2c). In summary, lithium metal does not homogeneously plate within the CNF membrane. Instead, there is a random distribution of metal clusters throughout the Li-CNF composite anode. A photograph of the composite anode macroscopically shows that the lithium metal distribution is heterogeneous, growing in large web-like patterns and in scattered metal clusters (Figure S3.4d). In contrast, we observe a homogeneous distribution of sodium metal throughout the CNF membrane. The topside of the Na-CNF anode (Figure 3.2e) shows a dense coating of sodium deposition, fully covering the CNF surface. The cross-section SEM image also shows that sodium metal is homogeneously coated throughout the CNF (Figure 3.2f). The bottom side of the composite anode also exhibits dense and relatively homogeneous sodium metal coating (Figure S3.5a). The pre-sodiation of the CNF through Na ion intercalation and adsorption during the early stage of electrodeposition (Figure 3.2d) likely increases the nucleation sites for sodium metal deposition.<sup>46</sup> The increased number of nucleation sites enhances the sodiophilicity of the CNF and improves the chemical affinity between sodium metal and the host material, resulting in the homogeneous coating of sodium metal on the CNF membrane.<sup>46</sup> The photograph of the Na-CNF surface also shows a homogeneous distribution of sodium deposition on the CNF membrane (Figure S3.5d).

TEM was performed after electrodeposition for the M-CNF composite anodes to ascertain the distinct plating behavior of both alkali metals. As expected, no distinctive coating of Li metal on the CNF surface was observed (Figure 3.2h). A thin layer is observed on the surface of the CNF (indicated by the arrow in Figure 3.2h), which may be a thin passivation layer resulting from the electrolyte decomposition. No pattern was observed from the fast Fourier transform (FFT) analysis

of the TEM image, suggesting that no detectable amount of crystalline compounds or lithium metal is present on the surface of the Li-CNF sample. Furthermore, the individual carbon fibers are free of noticeable deposition on the surface (Figure S3.6a-c) due to the weak affinity between lithium and the CNF, which is consistent with the above SEM results. In sharp contrast, after sodium electrodeposition, clear deposition has formed throughout the surface of multiple fibers (Figure S3.6d-f). Lattice fringes are observed in higher magnification of the Na-CNF. The FFT patterns detected are reminiscent of  $\text{Na}_2\text{CO}_3$  crystal planes (Figure 3.2i). The presence of  $\text{Na}_2\text{CO}_3$  is attributable to either SEI or the transformation of sodium metal during the TEM sample handling.

The SEI composition was investigated through XPS analysis of the composite anodes after deposition (Figure S3.7). For C 1s, O 1s, and Li/Na 1s, a stronger peak intensity for  $\text{Na}_2\text{CO}_3$  relative to  $\text{Li}_2\text{CO}_3$  is observed. This finding is consistent with the large presence of  $\text{Na}_2\text{CO}_3$  on the surface of the Na-CNF fibers from TEM analysis (Figure 3.2i). In the F 1s and Li 1s spectra, LiF is more abundant than  $\text{Li}_2\text{CO}_3$ . On the other hand, NaF is shown to have low intensity in the F 1s and to be less abundant than  $\text{Na}_2\text{CO}_3$  in the Na 1s spectrum. The increased amount of inorganic fluorinated species can improve the protective and ionic qualities in the SEI of the electrodeposited metals.<sup>47-49</sup> Even with the addition of FEC to the sodium electrolyte, the formation of  $\text{Na}_2\text{CO}_3$  during the electrolyte decomposition is greater than NaF. The prominent  $\text{CO}_3^{2-}$  peaks in the XPS spectra also confirm the increased amount of side reactions with the electrolyte during Na metal electrodeposition, inactivating a portion of the electrodeposited metal.

### 3.3.3 Electrochemical measurements of the Li/Na composite anodes

To further investigate the metal-host interaction, M-CNF cells were designed to establish the relationship between performance and the characteristics of the CNF host. Symmetric cells were cycled with a current density of  $0.5 \text{ mA cm}^{-2}$  for a  $0.5 \text{ mAh cm}^{-2}$  areal capacity. In these

symmetric cells, both electrodes were loaded with “lean” metal anode ( $3 \text{ mAh cm}^{-2}$ ) using the same electrodeposition process prior to the symmetric cell assembly. The Li-CNF symmetric cell sustained stable cycles for 160 hours before the cell overpotential gradually began to increase, with the cell shorting at 195 hours (Figure 3.3a). The Na-CNF symmetric cell, however, sustained stable cycling for over 2,000 hours, with minimal overpotential increase. In the zoomed-in profiles for selected cycles (Figure 3.3b-e), we observed the transformation of the voltage profile for the Li-CNF symmetric cell over the cycle life, while the Na-CNF symmetric cell remains fairly stable over the 2,000 hours. The Li-CNF symmetric cell has an initial overpotential of 30 mV, which is comparatively lower than that of the 75 mV of the Na-CNF symmetric cell. However, over time the Li-CNF symmetric cell fails to prevent side reactions with the electrolyte, causing the rapid consumption of lithium metal.<sup>14</sup> An unforeseen observation for the Na-CNF symmetric cell is that within the first 10 cycles, the primary cycling mechanism changed from metal stripping/plating to intercalation/surface adsorption (Figure S3.8).<sup>29</sup> The voltage profile during cycling also reflects this change if we compare the first cycle to the 50<sup>th</sup> cycle (Figure 3.3b,c). The relatively flat voltage curve that is associated with metal stripping/plating changes to a sloping profile that is maintained throughout the rest of its cycle life (Figure 3.3b-e). Such a change from stripping/plating to intercalation/surface adsorption may protect Na ions from being consumed by the electrolyte side reactions, thus allowing the Na-CNF symmetric cell to have a long cycle life.

The alkali metals were electrodeposited onto copper foil discs and cycled as M-Cu symmetric cells and M-CNF||M-Cu cells to determine the active role of the CNF host on the cycling performance of the composite anodes. Li-Cu symmetric cells only sustained 60 hours of stable cycling before succumbing to lithium metal consumption and shorting (Figure 3.3f). The addition of the CNF composite anode in the Li-Cu||Li-CNF cell prolongs the lifespan of the cell

approximately by 30 hours, but still succumbed to active metal depletion faster than the Li-CNF symmetric cell. As seen in the inset of Figure 3.3f, the Li-CNF symmetric cell has the lowest stripping/plating overpotential. The overlap between Li/Na p-orbitals and the  $\pi$  bond network of the crystalline domains of the CNF improves electron transfer throughout the electrode, lowering the overpotential needed for stripping/plating.<sup>27</sup> The cells that incorporate Na-Cu, however, show that the electrodeposited sodium metal fails to cycle more than 1-2 cycles before a sudden voltage increase, resulting in the cell shorting (Figure 3.3g). Even the inclusion of the Na-CNF anode failed to sustain stable cycling for more than 2 cycles when paired with Na-Cu (Figure 3.3g). The electrodeposited sodium metal on the Cu foil undergoes rapid consumption and reactions with the electrolyte, producing inactive sodium on the substrate. The Na-CNF symmetric cell improves the cycle life by a factor of over 2,000, which is primarily due to the change in Na-CNF interaction mechanism from plating/stripping to intercalation of Na ion into the crystalline domains of the CNF and adsorption onto the CNF surface.

The difference in the electrochemical stability of Li-CNF and Na-CNF composite anodes in Figures 3.3f and 3.3g led us to test the sustainability of the limited amount of electrodeposited metal by using a M||CNF configuration and performing plating/stripping cycles for an areal capacity 0.5 mAh cm<sup>-2</sup> of Li/Na metal onto the pristine CNF (Figure 3.3h,i). For the Li||CNF cell, over the period of 35 cycles, we observe high capacity reversibility and a lower hysteresis. For the Na||CNF cell, a much lower capacity reversibility is observed, and the capacity recovered from the first stripping cycle is approximately 60% of the plated capacity. The increase in voltage hysteresis over the 35 cycles is more drastic than the Li||CNF cell. With a smaller amount of metal deposited, we were able to more accurately investigate the electrochemical behavior and stability of the metal itself. The electrodeposited lithium metal, as we see in our case, is less reactive with the electrolyte

and has a higher degree of metal sustainability during the plating/stripping cycles, compared with electrodeposited sodium metal. Collectively, we further confirm, through Figures 3.3f-i, that the primary factor that the Na-CNF symmetric cells are able to sustain over 2000 hours (Figure 3.3a), without significant increase in polarization, is due to the intercalation and adsorption that Na ions undergo with the semi-crystalline lattice of the CNF, rather than the stability of the sodium metal itself.

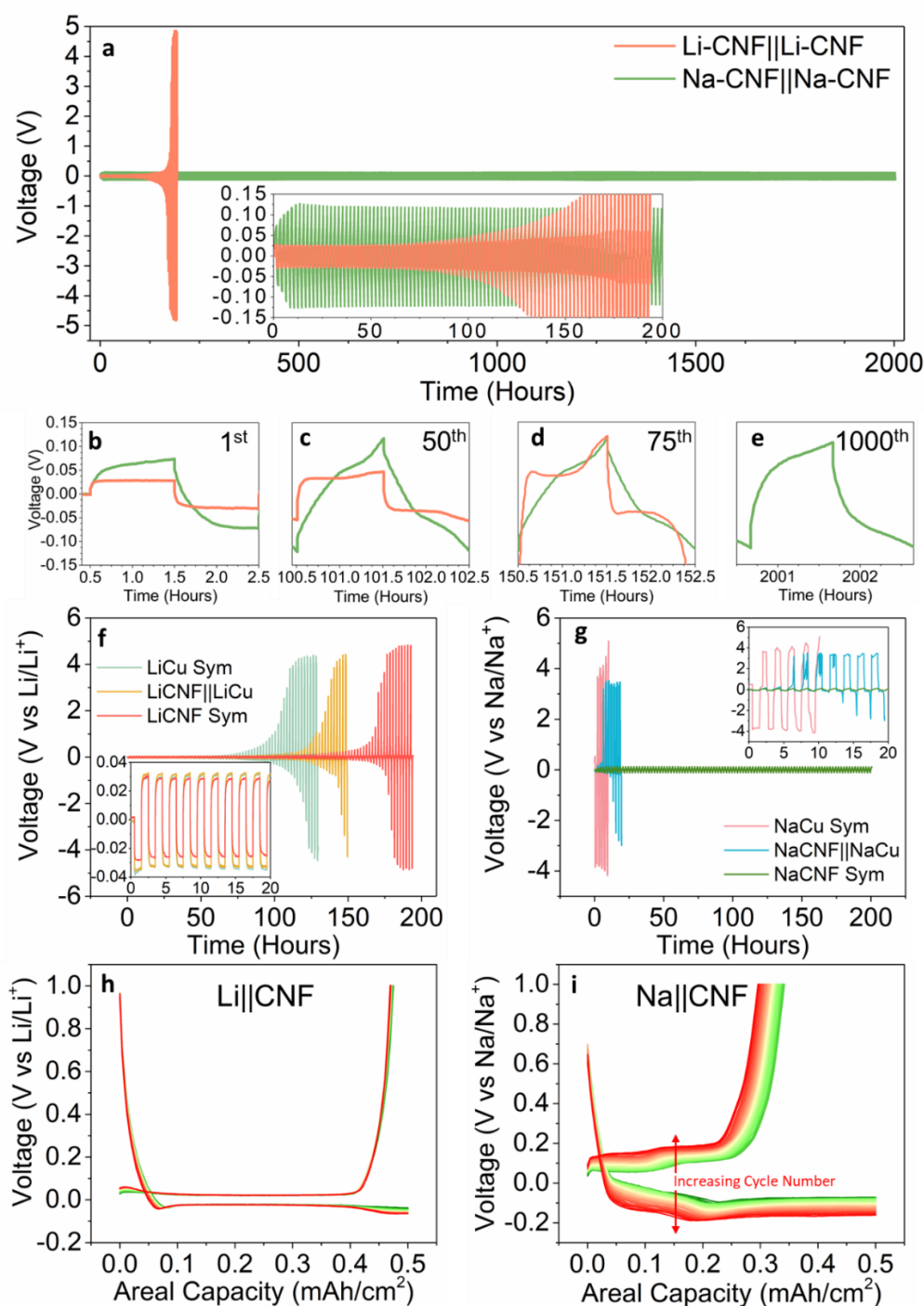


**Figure 3.3)** Electrochemical performance evaluation of Li-CNF and Na-CNF composite anodes. **a**) M-CNF||M-CNF symmetric cell performance for Li-CNF and Na-CNF anodes cycled at 0.5 mA cm<sup>-2</sup> for a 0.5 mAh cm<sup>-2</sup> areal capacity. The starting M loading in M-CNF is 3 mAh cm<sup>-2</sup>, which was electroplated in the M||CNF cell and collected for the symmetric cells. Insets of M-CNF symmetric cell cycling for the **b**) 1<sup>st</sup>, **c**) 50<sup>th</sup>, **d**) 75<sup>th</sup>, and **e**) 1000<sup>th</sup> cycles. Comparison between M-Cu||M-Cu, Mn-Cu||M-CNF, and M-CNF||M-CNF symmetric cycling performance for **f**) lithium and **g**) sodium. Plating/stripping of M||CNF with a current density of 0.5 mA cm<sup>-2</sup> and a cutoff areal capacity of 0.5 mAh cm<sup>-2</sup> over 35 cycles to test the stability of limited electrodeposited **h**) lithium and **i**) sodium metal. Cells for electrochemical testing were cycled at 22 °C.

### 3.3.4 Electrochemical impedance spectroscopy analysis of the SEI

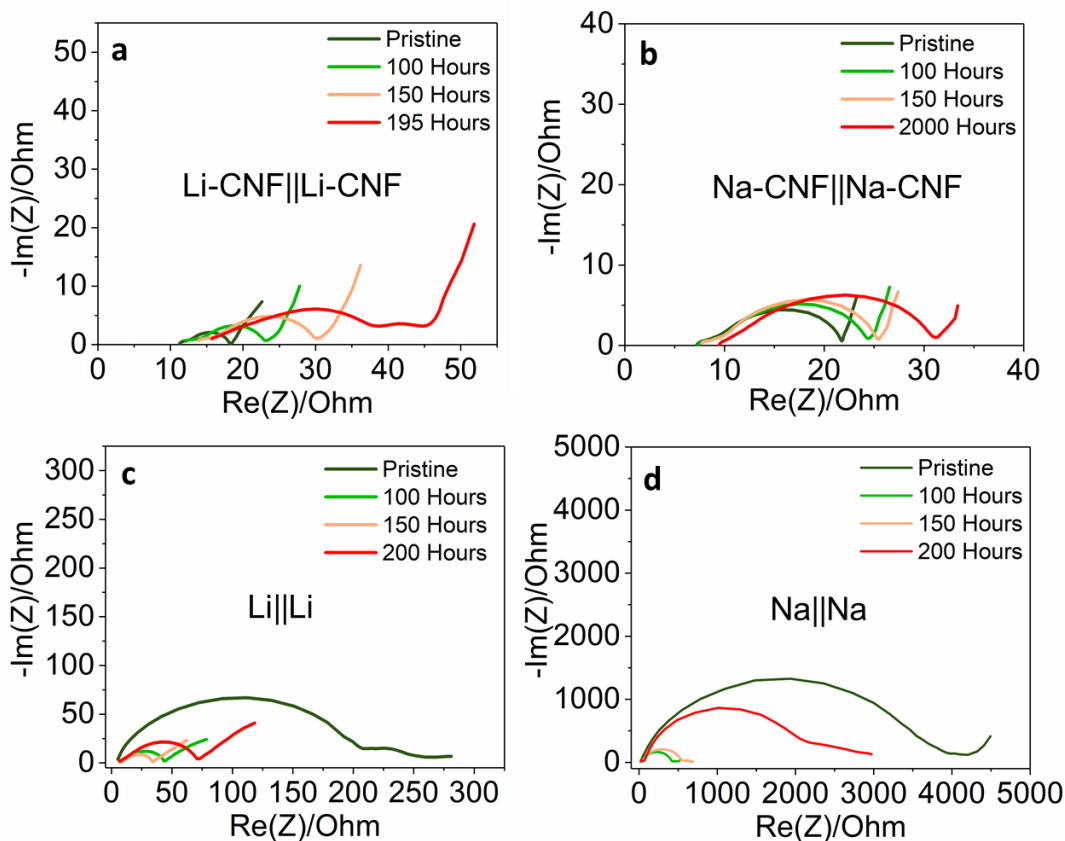


**Figure 3. 4)** Electrochemical impedance spectroscopy Nyquist plots of **a)** Li-CNF||Li-CNF, **b)** Na-CNF||Na-CNF, **c)** Li||Li metal, and **d)** Na||Na metal symmetric cells after stripping/plating cycles with a current density of  $0.5 \text{ mA cm}^{-2}$  and cutoff areal capacity of  $0.5 \text{ mAh cm}^{-2}$ .

After different stages of cycling, for the M-CNF||M-CNF and M||M symmetric cells, electrochemical impedance spectroscopy (EIS) was utilized to correlate the change in the cell internal resistance with the change in the cell overpotential during cycling, previously shown in Figure 3.3a. The cells were measured after full stripping/plating cycles at OCV to retain a nominal 0% state of charge. The pristine M-CNF||M-CNF symmetric cells show much smaller impedance than the pristine M||M symmetric cells. This observation may be explained by the fact that SEI layers are formed on the composite anodes during the electrodeposition to prepare M-CNF electrodes, which may drastically improve the initial electrode-electrolyte interface. The pristine

Li-CNF and Na-CNF symmetric cells are similar in their impedance values, with the main distinction that Na-CNF has a slightly larger semi-circle related to higher charge transfer resistance, and Li-CNF has a more prominent tail end slope attributed to the solid-state mass transfer resistance in the active material.<sup>50</sup> With increasing cycle time, the impedance of the Li-CNF symmetric cell increases more rapidly (Figure 3.4a), matching the increase in overpotential during cycling (Figure 3.3a). The formation of second semi-circle corresponds to the depletion of active lithium metal and increase in SEI layer thickness (Figure 3.4a).<sup>50</sup> While the Na-CNF cell starts off with a slightly higher impedance, it maintains considerable stability over 2,000 hours. The slow increase and stability of the impedance values are consistent with the highly stable cycling performance and overpotential in Figure 3.3a. The impedance only increased slightly after 2000 hours of cycling, which is likely attributed to the highly stable SEI and reversibility of Na<sup>+</sup> intercalation/de-intercalation within the semi-crystalline CNF.

The pristine full metal symmetric cells have large initial impedance due to high interfacial resistance without the presence of a formed SEI on the metal surface to improve electrode-electrolyte interaction (Figures 3.4c,d). After cycling for 100 hours, the SEI is fully formed and the impedance for both lithium and sodium metal symmetric cells were significantly reduced. Over 200 hours, the impedance values gradually increase for lithium (Figure 3.4c). However, more notable impedance growth is observed for the sodium symmetric cell after cell shortage (Figure 3.4d and Figure S3.9). The SEI of the full metal symmetric cells are unstable and unable to accommodate the volume fluctuation of the constant heterogeneous plating/stripping cycles, which may lead to the formation of cracks in the SEI and increasing amounts of side reactions between the electrolyte and freshly exposed metal surfaces.<sup>51,52</sup> Therefore, compared to the full metal

anodes, the composite anodes have a much lower impedance due to the enhanced stability and local charge homogeneity potentially benefited from the  $\pi$ - $\pi$  network in the CNF.<sup>53</sup>

### 3.3.5 Probing alkali ion interactions through electrochemical kinetic analysis

Through symmetric electrochemical cycling and EIS analysis, a disparity in the performance and host-guest interactions of lithium and sodium metal composite anodes was observed. Although we observed carbon  $d_{002}$  expansion after lithium and sodium electrodeposition, the sodium composite anode has exhibited superior electrochemical stability and performance. Further electrochemical diagnostics was performed to probe the chemical interaction between the alkali metal and the CNF. To determine the degree and reversibility of the Li/Na ion interaction with the pristine CNF, cyclic voltammetry (CV) was utilized with a scan rate of  $0.1 \text{ mV s}^{-1}$  between 0.01-3 V (Figure 3.5a,b). Magnified profiles at a lower potential window are shown in Figure 3. S10 (Supporting Information). During the first reduction process for the Na||CNF cell, the two reduction peaks  $\sim 0.5 \text{ V}$  and  $0.25 \text{ V}$  (indicated by the arrows in Figure 3.5a and Figure S3.10a) are associated with the electrolyte decomposition and SEI formation. Another small reductive peak below  $0.1 \text{ V}$  is attributed to  $\text{Na}^+$  intercalation into carbon crystalline domains.<sup>29</sup> On the subsequent oxidation process, the small oxidative peak observed is related to the de-intercalation of  $\text{Na}^+$  from the crystalline domain.<sup>29</sup> A new reductive peak is observed during the second reductive process  $\sim 0.38 \text{ V}$ , matching the plateaus observed during electrodeposition (Figure 3.2d). During the third cycle, the reductive peak at  $0.38 \text{ V}$  becomes much less prominent, indicating subdued side reactions of the electrolyte. For the Li||CNF cell, a small reduction peak  $\sim 0.8 \text{ V}$  on the first discharge cycle shows that the initial side reactions for the SEI formation are less severe compared to what we observe in the Na||CNF cell. The Li||CNF cell has prominent oxidation/reduction peaks

$\sim 0.1$  V and are highly stable over the three CV cycles, which is related to Li ion adsorption onto the CNF surface.<sup>45</sup>

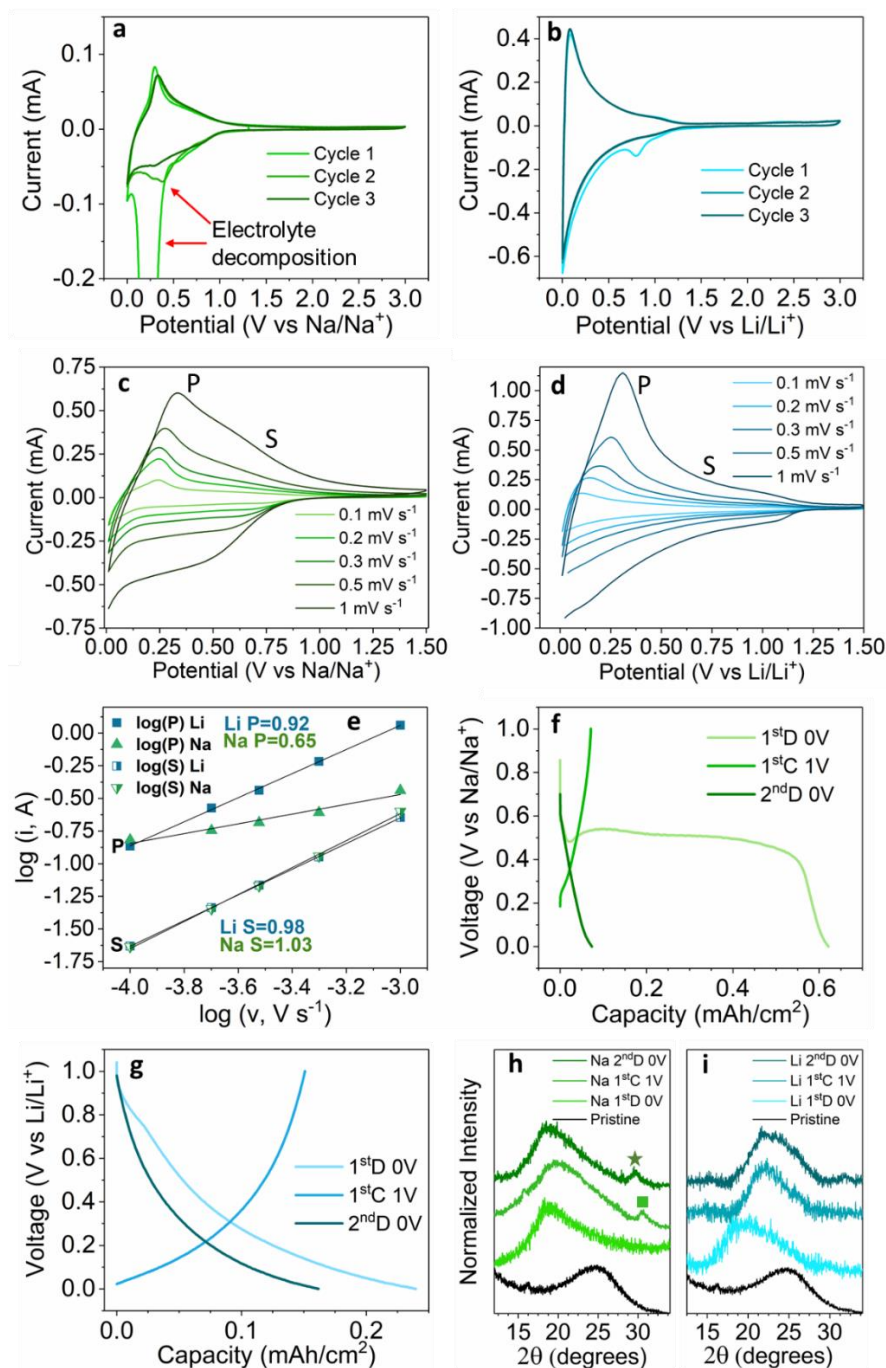


**Figure 3.5)** Electrochemical investigation of the interaction between Na/Li ion and the pristine CNF. Cyclic voltammetry (CV) of **a)** Na||CNF and **b)** Li||CNF at a scan rate of  $0.1 \text{ mV s}^{-1}$  and a voltage range of  $0.01 - 3 \text{ V}$ . CV at different scan rates for **c)** Na and **d)** Li. **e)** The corresponding correlation between the scan rate and peak current at

low potential (peak (P), ~0.1 V) and at high potential (slope (S), ~0.75 V). M||CNF half-cell charge (C) and discharge (D) voltage profile of **f**) Na and **g**) Li from 0.01 – 1 V with a current density of 0.05 mA cm<sup>-2</sup>. XRD of the CNF anode after charge/discharge for **h**) Na and **i**) Li. The peaks marked with the star and box are attributed to sodium metal formation and electrolyte decomposition, respectively.

The kinetic analysis of CV curves at different scan rates has been proven to be a useful method for determine the mechanism of the host-ion interactions.<sup>29,54</sup> By using a curve fitting equation  $i = av^b$  we can understand the relation between scan rate ( $v$ ) and the measured peak current ( $i$ ). The b-value is ascertained from the slope of  $\log(v)$  and  $\log(i)$ . A b-value close to 0.5 is indicative of a more diffusion-controlled reaction, such as intercalation, and a b-value of 1 indicates fast kinetics and primarily surface mass transport such as surface adsorption.<sup>29,54</sup> The scan rates used range from 0.1 mV s<sup>-1</sup> to 1 mV s<sup>-1</sup>. The sharp peak at ~0.1 V corresponds to the charge/discharge plateau region below 0.1 V labeled (P) and ~0.75 V for the slope region labeled (S) (Figures 3.5c-d). The fitted b-values for the P region for lithium is 0.922 and 0.653 for sodium, with an R<sup>2</sup> of 0.99 and 0.97, respectively, (Figure 3.5e). The b-values indicate that at low voltage the primary ion-host interaction for lithium is surface adsorption and for sodium is bulk intercalation into the crystalline domain of the CNF. For the S region, i.e., at higher voltage, the b-value for lithium is 0.98 and sodium is 1.03, with an R<sup>2</sup> of 0.99 for both lithium and sodium, representing that both metal ions undergo surface adsorption with the CNF. These results show that Li-CNF interaction is primarily surface adsorption, whereas Na<sup>+</sup> undergoes both surface adsorption and intercalation into the CNF crystalline domains.

The degree and reversibility of ion intercalation was then tested by cycling M||CNF cells at a low current density of 0.05 mA cm<sup>-2</sup> between 0.01-1 V (Figure 3.5f,g) followed by *ex-situ* XRD of the cycled CNF anodes (Figures 3.5h,i). When cycled at the lower current density, a considerable change in the discharge voltage profile is observed for both Li||CNF and Na||CNF cells, compared to the electrodeposition profiles in Figure 3.2. During the first discharge for the

Na||CNF cell, a long plateau is observed (Figure 3.5f). The plateau is related to a significant amount of side reactions and SEI formation, similar to the large current peak in the initial CV reduction process (Figure 3.5a). On the subsequent charging cycle, a significant irreversible capacity is observed, also indicating extensive side reactions from the SEI formation during the first discharge. The second discharge shows similar capacity to the charging step and better Coulombic efficiency. The first discharge for Li||CNF has a large sloping discharge curve (Figure 3.5g), compared to the quick voltage drop to 0 V observed during electrodeposition (Figure 3.2a). Overall, compared to the Na||CNF cell, the Li||CNF cell has less severe initial electrolyte side reactions, better capacity reversibility, and higher capacity, similar to other reports investigating lithium and sodium ion performance with carbonaceous anodes.<sup>26,27,55</sup> The sloping profiles for the Li||CNF cell during discharge, even at a low current density, further support that the surface adsorption is the predominant interaction mechanism between Li ion and the CNF. This result is consistent with the CV kinetics analysis (Figure 3.5e).

The cycled CNF anodes were retrieved and ex-situ XRD was performed to observe the reversibility of Na ion and Li ion intercalation/deintercalation within the crystalline domain. The  $d_{002}$  peak exhibits a left shift in the XRD pattern, corresponding to an interlayer  $d_{002}$  expansion by 1.16 Å, after the Na||CNF cell is discharged in the first cycle (Figure 3.5h). After the subsequent charging step, a slight right shift in the XRD pattern is observed, depicting incomplete removal of  $\text{Na}^+$  from the lattice and the formation of a new peak  $\sim 31^\circ$ , reported to be related to the decomposition of the electrolyte.<sup>29</sup> The XRD pattern after the second discharge highlights the reversibility of the ion intercalation with the  $d_{002}$  peak shifting back to an overlapping position, consistent with the pattern after the first discharge. A new peak developed after the second discharge at  $29.8^\circ$  related to formation of sodium metal.<sup>39</sup> A noticeable difference is shown in the

XRD patterns between sodium and lithium after cycling (Figure 3.5h,i). We observe a greater degree of a right shift for the corresponding  $d_{002}$  peak after the Li||CNF cell is charged, showing that Li ion has a greater extent of deintercalation. However, in the second discharge cycle, there is no discernable shift in the  $d_{002}$  peak, which indicates that Li ion cannot be re-intercalated into the crystalline domain of the CNF.

In summary, the electrochemical and structural analyses highlight the different interaction mechanisms of Li ion and Na ion with the CNF host. The primary interaction mechanism for Li ion is the surface adsorption, whereas Na ion has a combined adsorption-intercalation mechanism. The intercalation of Na ion into the crystalline domain promotes the long cycle life of the Na-CNF composite anode (Figure 3.3a). The CNF host may act as a “scavenger” to protect the intercalated Na ions from being consumed by side reactions with the electrolyte. When the electrodeposited metallic sodium is depleted, the Na-CNF composite anode can still continue stable cycling because of the availability of the intercalation mechanism. However, the Li-CNF composite anode begins to fail rapidly after undergoing lithium metal depletion.

### 3.3.6 Full cell cycling

The “lean” metal composite anodes were then paired with  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC 622) and  $\text{NaNi}_{0.33}\text{Fe}_{0.3}\text{Mn}_{0.33}\text{Ti}_{0.04}\text{O}_2$  (NFM 333) cathodes, respectively, to test the practical viability of the composite anodes in full cells. The cells containing NMC were cycled between 2.5-4.5 V vs.  $\text{Li/Li}^+$  and the cells containing NFM 333 were cycled between 2.0-4.0 V vs.  $\text{Na/Na}^+$ . These are common cutoff voltages used for these materials in the literature.<sup>56-59</sup> The typical galvanostatic discharge profiles are shown in Figure S3.11 (Supporting Information). The initial discharge capacities in both cells match well with the values reported in the literature.<sup>56-59</sup> Initially, similar cycling performance is observed for both full cells (Figure 3.6a). At 140 cycles, the Li-CNF full

cell begins to undergo rapid cell failure, quickly depleting the limited electrodeposited lithium metal. The Li-CNF full cell retains ~10% capacity for the rest of the long-term cycles. In contrast, Na-CNF maintains a 75% retention after 500 cycles, which is competitive to the sodium foil cell (80%), and slightly higher than the Na-HC composite anode (73%) after 500 cycles (Figure 3. S3.12a).

To determine whether the high upper cutoff voltage (4.5 V vs.  $\text{Li/Li}^+$ ) plays a role in accelerating the consumption of Li metal in the Li-CNF composite anode, the upper cutoff voltage was lowered to 4.3 V (Figure S3.13a). The % capacity retention profile is similar to the full cell with an upper cutoff voltage of 4.5 V. These results indicate that the upper cutoff voltage or the amount of cathode capacity that is cycled, does not play a significant role in the lifespan of the cell containing the Li-CNF composite anode. At a 2C rate we observed that the capacity fade of the Li-CNF full cell is more severe (Figure 3.6d). The capacity retention of the Na-CNF full cell at 2C increases to 87.5% after 500 cycles and outperforms the cell containing the pure sodium metal foil anode (80%) (Figure S3.12c).

Both Li- and Na-CNF full cells maintain a ~99.5-99.9% CE during their stable cycling periods. When the Li-CNF full cell begins the state of rapid cell failure, a decrease in the CE is observed, dropping rapidly to 80% for 1C and 89% for 2C before developing an erratic and unstable behavior. The CE for Na-CNF remains fairly stable for the entirety of the 500 cycles (Figure 3.6b). The average voltage delivered by the composite anode full cells shows good stability and consistency, comparable with the alkali metal half cells (Figures 3.6c, f and Figure S3.14). During the stable cycling phase for all Li-CNF full cells, there was a minimal decrease in the average voltage. Similar to the trend observed for the CE in Figure 3.6b, a sharp fluctuation in the average voltage signaled the stage of rapid cell failure, followed by unstable cycling behavior in

subsequent cycles. The Na-CNF full cell remained stable over its 500 cycles and is consistent with Na metal half cells (Figures 3.6c,f and Figure S3.14b,c).

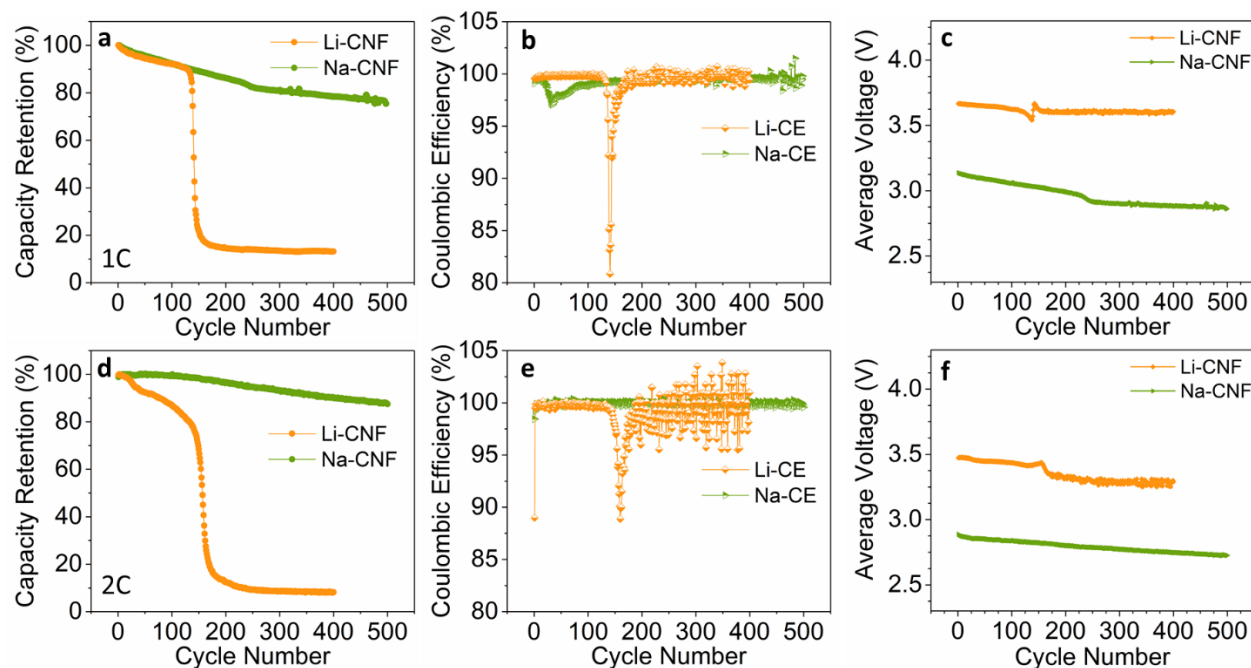


**Figure 3.6)** Electrochemical performance of the full cells containing the Li-CNF and Na-CNF composite anodes. The configurations are  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2\|\text{Li-CNF}$  and  $\text{Na}_{0.96}\text{Ni}_{0.33}\text{Fe}_{0.33}\text{Mn}_{0.33}\text{Ti}_{0.04}\text{O}_2\|\text{Na-CNF}$ . The voltage window of the lithium full cell is 2.5 – 4.5 V vs.  $\text{Li/Li}^+$  and the voltage window of the sodium full cell is 2.0 – 4.0 V vs.  $\text{Na/Na}^+$ . The cells are cycled at 1C (**a-c**), and 2C (**d-f**). (**a,d**) Percent capacity retention, (**b,e**) Coulombic efficiency, and (**c,f**) average voltage. Cells for electrochemical testing were cycled at 22 °C. C rate for Li and Na full cells is the time required to fully charge/discharge cell relative to a specific current density.

To understand the role of the electrodeposited lithium and sodium, full cells were assembled using the pristine CNF as the anode (Figure S3.15). Both NMC622 and NFM333 cells exhibit poor cyclability with the pristine CNF anode. The NMC622 cell can sustain  $24 \text{ mAh g}^{-1}$  capacity during its cycle life. The NFM cell initially has  $20 \text{ mAh g}^{-1}$  and quickly fades to  $5 \text{ mAh g}^{-1}$ . When these cathodes are paired with a graphite or hard carbon anode, reasonable cell capacity can be obtained. Collectively, these results suggest that the pre-lithiation and pre-sodiation of the CNF through electrodeposition directly contribute to the battery performance of the composite anodes in full cells.

### 3.4 Conclusion

Through using a semi-crystalline CNF material, we have demonstrated the fundamental effect that the structural characteristics of the CNF has on the intercalation, electrodeposition, and cycling behavior between lithium/sodium metal and the CNF host. Sodium metal has been shown to plate uniformly throughout the CNF host material, and lithium metal is unable to coat the CNF and instead forms a heterogenous distribution of metal clusters along the CNF surface. However, the instability of the electrodeposited sodium metal causes the Na-CNF to undergo change in its primary cycling mechanism from metal stripping/plating to sodium ion intercalation/de-intercalation. The (de)intercalation mechanism enables Na-CNF to sustain 2,000 hours of symmetric cycling with no significant increase in overpotential or impedance and to retain 75% and 80% capacity retention at 1C and 2C after 500 full cell cycles, respectively. The electrodeposited lithium metal has better cyclability and lower overpotential, but the inability to intercalate into the CNF crystal structure limits the effectiveness of the composite anode. Li-CNF can only sustain 160 hours of stable symmetric cell cycling, and 140 and 160 full cell cycles at 1C and 2C, respectively, before undergoing active material depletion and suffering from significant polarization. The semi-crystalline carbon structure with a  $d_{002}$  of 3.59 Å accommodates reversible intercalation/de-intercalation and adsorption for Na ions, allowing for long-term, stable performance for Na-CNF. However, Li ion interaction is primarily limited to surface adsorption. The CNF host may act as a “scavenger” to protect the intercalated Na ions from being consumed by side reactions with the electrolyte, allowing for the enhanced stability to enable stable, long term cycling. Through our characterization analysis, we can conclude that the surface functionalization and ability to adsorb and/or intercalate is a crucial aspect in the -philic or -phobic relationship between the alkali metal and the substrate. The optimization parameters of the carbon

substrate's crystallinity to improve the ionic and metal-host interaction will differ for lithium and sodium. This study will help guide the direction for improved alkali composite anode designs *via* crystalline structure optimization of the carbon host material.

## 3.5 Experimental Section

### 3.5.1 Materials Synthesis

For the carbon nanofiber preparation, walnut shell (*Juglans Sigillata*) was ground (>100 mesh) and dried in an oven at 80 °C. The mixture of walnut shell powder, phenol, and sulfuric acid (concentrated 98%) at a mass ratio of 1:4:0.03 was liquefied for 2 hours at 150 °C. Subsequently, the mixture was poured into dioxane/water (8/2, v/v) at a volume ratio of 1/15. The diluted solution was altered and concentrated under reduced pressure to obtain impurity-free liquefied products. The liquefied phenol formaldehyde resin (LPF) was synthesized by formaldehyde (F) and liquefied products (LP) with sodium hydroxide (NaOH) as a catalyst (molar (LPF), LP, NaOH solution and 80% of the total F were added into ratio,  $F/LP = 1.45/1$ ,  $NaOH/LP = 0.2/1$ ). In synthesizing resin (LPF), LP, NaOH, and 80% of the total F were added into a three-neck flask. The solution was heated to 82 °C for 60 min. After, the remaining 20% of F was added. The reaction temperature was increased to and kept at 87 °C and stirring for 120 min. The solution was cooled to room temperature. Subsequently, the synthesized LPF was diluted to 18 wt% in solid content with distilled water and 12 wt% polyvinyl alcohol (PVA) aqueous solution added to the LPF to adjust the electro-spinability (mass ratio of LPF/PVA  $\frac{1}{4}$  8/2). The mixed solution stirring was continued for 2 h. Electrospun nanofibers were prepared using an electrospinning device (ET-2535H, Ucalery), which consisted of a high voltage power supply, a syringe pump, and a roller (covered with aluminum foil) connected to the negative pole for collecting the fibers. The spinning solution

was loaded into a 5 mL plastic syringe with a 22-gauge needle connected to the positive pole of a voltage generator. During spinning, the distance was adjusted to 25 cm between the tip of needle and the roller, an operating voltage was ranged from 16 kV and the feeding rate of spin was maintained at 0.05 mL min<sup>-1</sup>. The carbon nanofibers were fabricated by one-step carbonation at 1800 °C at a rate of 5°C min<sup>-1</sup> and held for 60 min in a nitrogen atmosphere.

The LiNi<sub>0.6</sub>Mn<sub>0.2</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode materials were synthesized using a co-precipitation method followed by calcination. The acid metal solution was prepared using 0.6 M NiSO<sub>4</sub>·6H<sub>2</sub>O (Sigma Aldrich, 99.99%), 0.2 M MnSO<sub>4</sub>·H<sub>2</sub>O (Sigma Aldrich, 99%) and 0.2 M CoSO<sub>4</sub>·7H<sub>2</sub>O (Sigma Aldrich, 99%) as the raw materials dissolved in 100 mL H<sub>2</sub>O. The transition metal solution, starting solution (40 mL NaOH and NH<sub>3</sub>·H<sub>2</sub>O aqueous solution with a molar ratio NaOH/NH<sub>3</sub> = 1.2, with the pH value was adjusted to 10.5) and base solution (100 mL NaOH and NH<sub>3</sub>·H<sub>2</sub>O aqueous solution with a molar ratio NaOH/NH<sub>3</sub> = 1.2) were made and separately stored under N<sub>2</sub> protection. The transition metal solution and base solution were simultaneously pumped into the starting solution at a drop rate of 2 mL min<sup>-1</sup> with continuously stirring at 50 °C under the N<sub>2</sub> protection. The drop rate of the base solution was frequently tuned to keep the pH at 10.5 ± 0.2. The precipitate was collected, washed, and filtered with DI water and dried in a vacuum oven overnight at 100 °C. The dried precursor was then mixed with LiOH thoroughly and calcined under air flow (2 L min<sup>-1</sup>) at 725 °C for 6 hours.

The NaNi<sub>0.33</sub>Fe<sub>0.3</sub>Mn<sub>0.33</sub>Ti<sub>0.04</sub>O<sub>2</sub> cathode materials were synthesized using a co-precipitation method followed by calcination. Two separate acidic metal solutions were prepared. First, the acidic metal sulfate solutions were prepared using 0.033 M NiSO<sub>4</sub>·6H<sub>2</sub>O (Sigma Aldrich, 99.99%), 0.030 M FeSO<sub>4</sub> · 7H<sub>2</sub>O (Sigma Aldrich, 98%), and 0.033 M MnSO<sub>4</sub>·H<sub>2</sub>O (Sigma Aldrich, 99%) as the raw materials dissolved in 100 mL H<sub>2</sub>O. The other acidic solution consisted of 0.004

m TiOSO<sub>4</sub> dissolved in 100 mL water. The starting solution (40 mL NaOH and pH value adjusted to 10.5 using sulfuric acid) and base solution (100 mL NaOH/NH<sub>3</sub> · H<sub>2</sub>O aqueous solution with a molar ratio of NaOH/NH<sub>3</sub> = 2.4 (0.2 m NaOH). The transition metal solution and base solution were simultaneously pumped into the starting solution at a drop rate of 2 mL min<sup>-1</sup> with continuously stirring at 55 °C under N<sub>2</sub> protection. The acid TiOSO<sub>4</sub> solution was pumped into the acidic NiSO<sub>4</sub>/FeSO<sub>4</sub>/MnSO<sub>4</sub> solution at a rate of ≈ 1 mL min<sup>-1</sup>. The drop rate of the base solution was frequently tuned to keep the pH at 10.5 ± 0.2. The precipitate was collected, washed, and filtered with DI water and dried in a vacuum oven overnight at 100 °C. The dried precursor was then thoroughly mixed with nanosized Na<sub>2</sub>CO<sub>3</sub> (the molar ratio of TM/Na was 1:1.08), transferred into a box furnace and calcined at 850 °C for 10 h.

### 3.5.2 Materials Characterization

The morphologies of the materials were investigated using a scanning electron microscope (SEM) (LEO FESEM) at an accelerating voltage of 5 kV. TEM images were acquired on a JEOL 2100 TEM operated at 200 keV. N<sub>2</sub> adsorption-desorption was acquired on a Micromeritics-3Flex surface characterization analyzer. The surface area was calculated using a Brunauer-Emmett-Teller (BET) method in the linear range of P/P<sub>0</sub> = 0.01-0.1. XPS characterization was performed on a PHI VersaProbe III scanning XPS microscope using monochromatic Al K-alpha X-ray source (1486.6 eV). Samples were transferred from an Ar-filled glove box to the XPS ultrahigh vacuum chamber via a vacuum transfer vessel. All binding energies were referenced to C-C peak at 284.8 eV. XRD characterization was performed on Rigaku Miniflex II. Electrodes were retrieved inside Ar-filled glovebox and sealed in Kapton tape.

### 3.5.3 Electrochemical Characterization

The NMC composite electrode was prepared with 90% active material, 5% carbon black, and 5% poly(vinylidene difluoride) (PVDF) binder. The NFM electrode was prepared with 85% active material, 10% carbon black, and 5% PVDF binder. The PVDF solution was prepared with N-methyl 2-pyrrolidone (NMP) as the solvent. The cathode slurry for NMC and NFM was prepared by mixing the PVDF solution with the respective cathode active material and carbon black powder. The slurry was mixed in a Speedmixer for a set amount of time to ensure a homogeneous mixture. The slurry was casted onto carbon-coated Al foil using the doctor blade casting method at 70 °C. The dried casted electrode was cut to 10 mm diameter electrodes and dried in a vacuum oven overnight at 120 °C. The dried electrodes were stored in an Ar-filled glovebox. Total active material mass loading for both NMC and NFM cathodes was  $\sim 4 \text{ mg cm}^{-2}$ . 1C was defined as fully charging the cathode in 1 h corresponding to a specific current density of 200 mA g<sup>-1</sup> for the NMC and 120 mA g<sup>-1</sup> for the NFM cathodes. Metal composite anodes were prepared through electrodeposition. Hard carbon and graphite electrode were prepared by mixing 90% active material with 10% PVDF using NMP as the solvent. The slurry was mixed in a Speedmixer and casted onto copper foil using the doctor blade method and dried at 70 °C. The resulting electrode was cut into 16 mm discs and dried in a vacuum oven overnight for 120 °C and subsequently placed into an Ar-filled glovebox. The metal-CNF composite anode was prepared with an adhered a pristine CNF disc (2 cm<sup>2</sup>) to a copper current collector as the positive electrode and a lithium or sodium foil disc (2 cm<sup>2</sup>) as the negative electrode in a coin cell (CR 2032 model). The current density used for electrodeposition was 0.25 mA cm<sup>-2</sup> for a total areal capacity of 3 mAh cm<sup>-2</sup>. Graphite and HC composite anodes followed the same electrodeposition procedure as the CNF composite anodes. The NMC and NFM cathodes were combined with the Li/Na-CNF

composite anode with glass fiber separator. Lithium cells used 1 M LiPF<sub>6</sub> EC/EMC electrolyte (Gotion, LP57) with 2% VC wt% (Sigma Aldrich, 98%). Sodium cells used 1 M NaPF<sub>6</sub> (98%, Sigma Aldrich) dissolved in a PC solvent (Gotion) with 2% FEC wt% (Sigma Aldrich, 99%). All coin cells were assembled in an Ar-filled glovebox. LANDT battery testers and software was utilized to collect all full cell, half cell, and symmetric cell cycling data. Cyclic voltammetry measurements were performed on a Princeton Applied Research VersaSTAT 4. Electrochemical impedance spectroscopy measurements were performed on using a Biologic SP-50 potentiostat. All electrochemical coin cell testing was performed at 22 °C.

### **3.6 Acknowledgements**

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### 3.7 Supporting Information

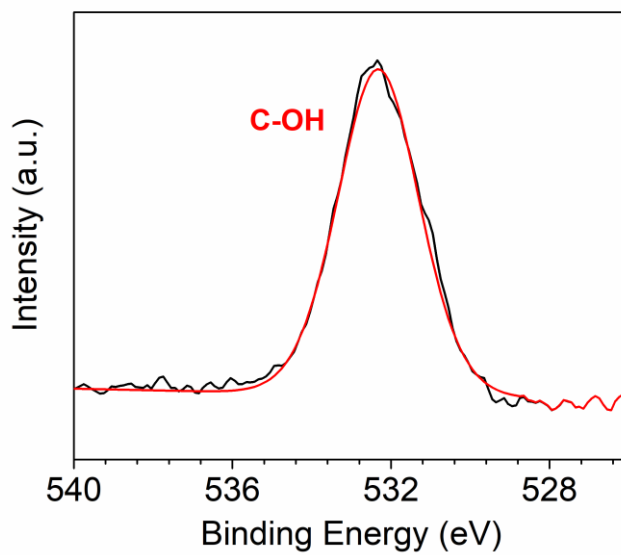


**Figure S3.1)** O 1s XPS for pristine carbon nanofiber.

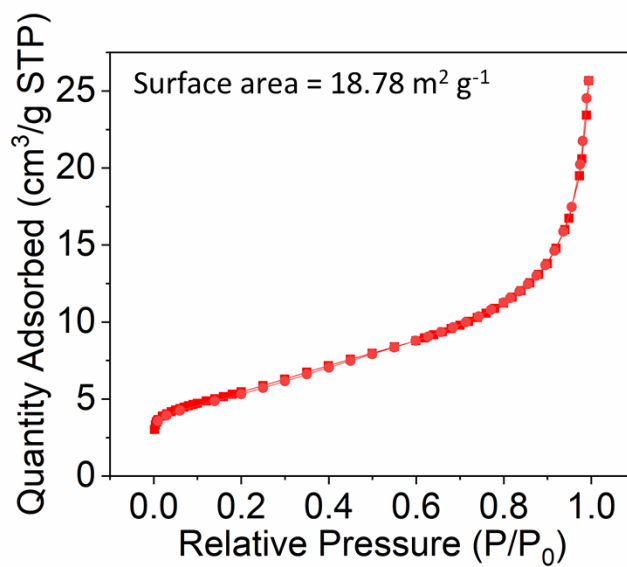


**Figure S3.2)** N<sub>2</sub> (77k) adsorption-desorption isotherm for pristine carbon nanofiber.

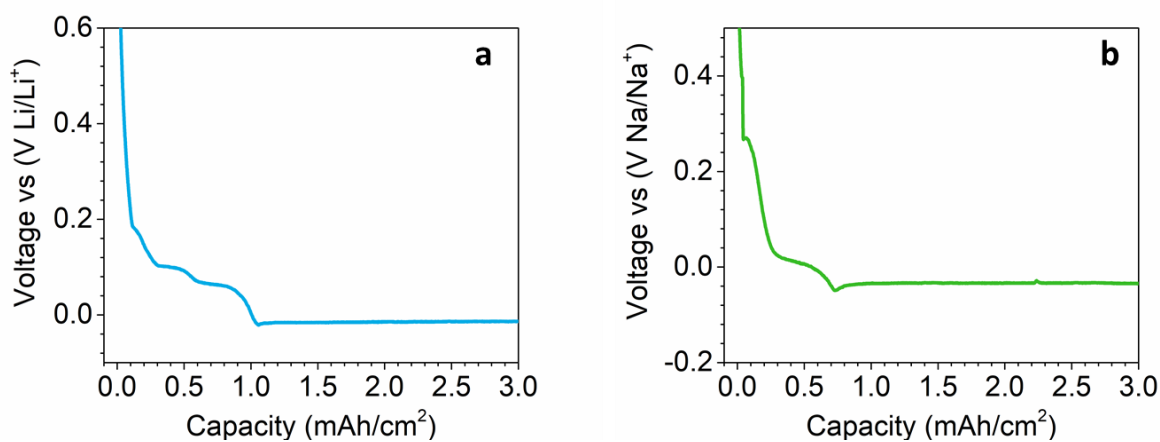


**Figure S3.3)** Electrodeposition voltage profiles for a) Li-graphite and b) Na-Hard Carbon composite anodes.

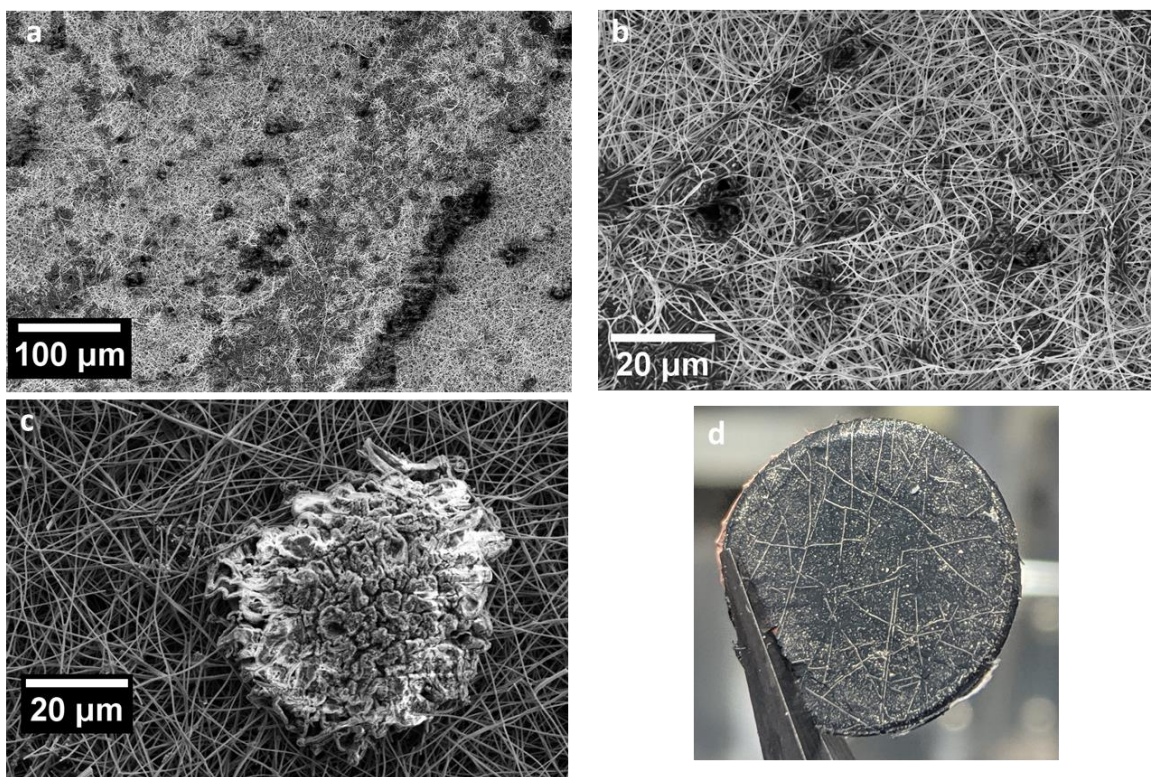


**Figure S3.4) (a-d)** Images of Li-CNF after  $3 \text{ mAh cm}^{-2}$  electrodeposition a) Low magnification SEM image on bottom side of Li-CNF. b) High magnification SEM image on bottom side of Li-CNF. c) High magnification SEM image of large Li metal cluster on top side of Li-CNF and d) photo image of Li-CNF.

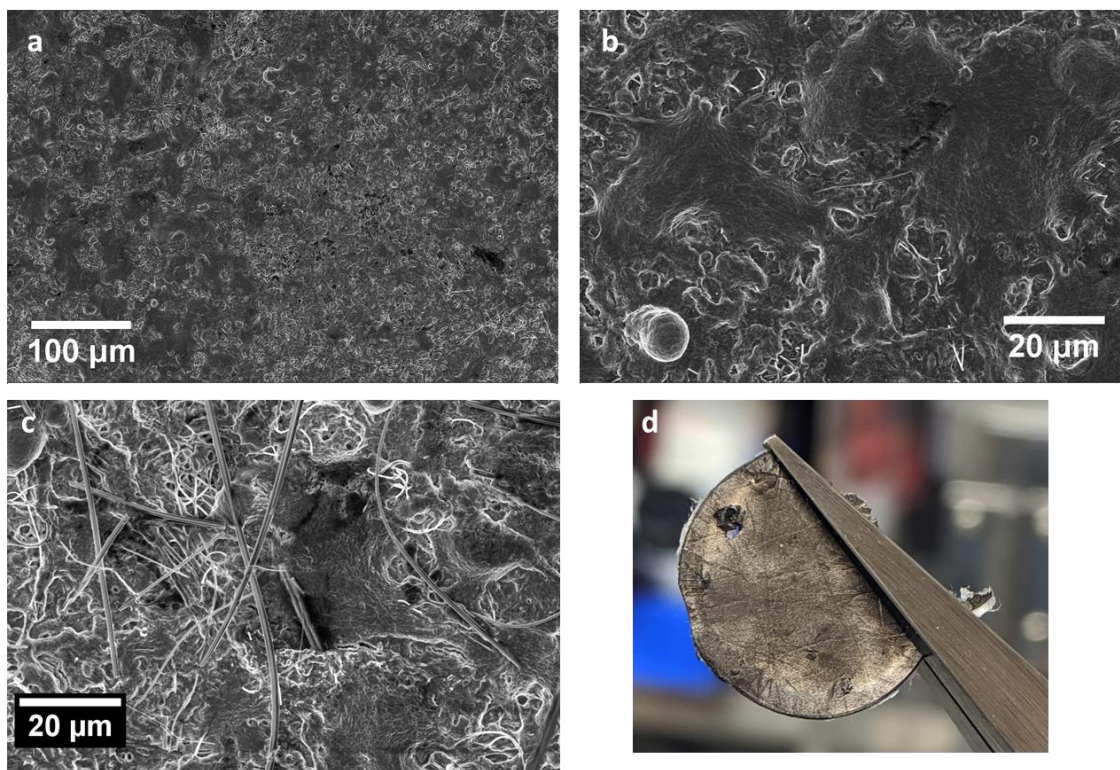


**Figure S5)** (a-d) Images of Na-CNF after 3 mAh cm<sup>-2</sup> electrodeposition. a) Low magnification SEM image on bottom side of Na-CNF. b) High magnification SEM image on bottom side of Na-CNF. c) High magnification SEM image of large homogeneous plating on top side of Na-CNF. d) Photo image of Na-CNF

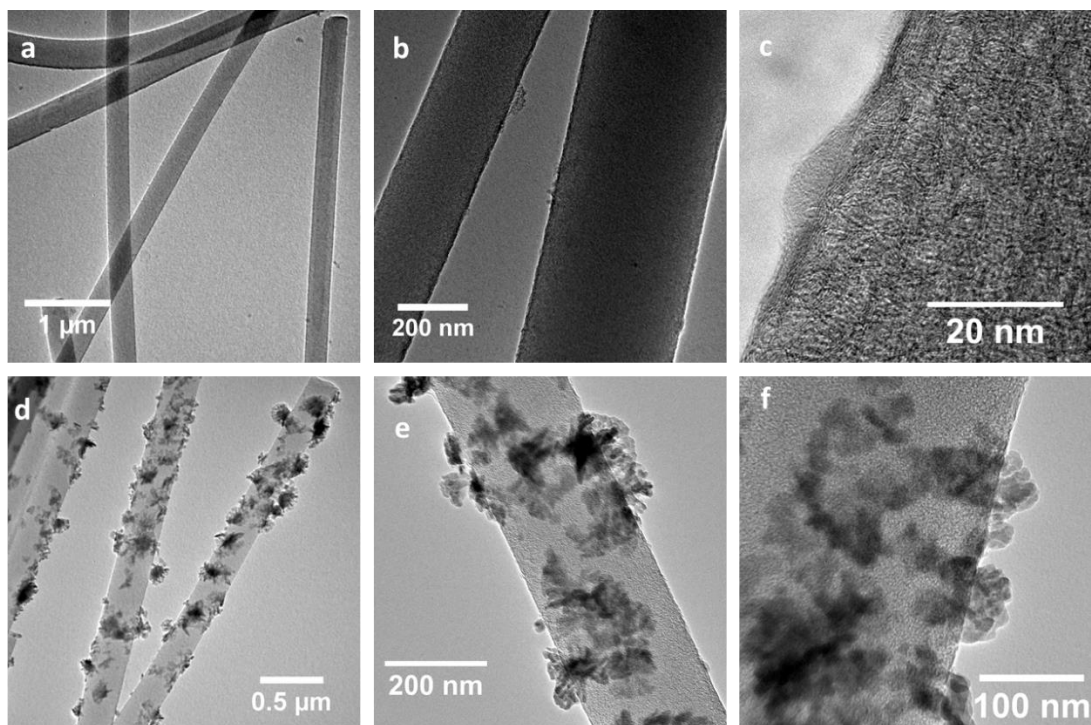


**Figure S3.6)** TEM images for Li-CNF (a-c) and Na-CNF(d-f) at varying magnifications.

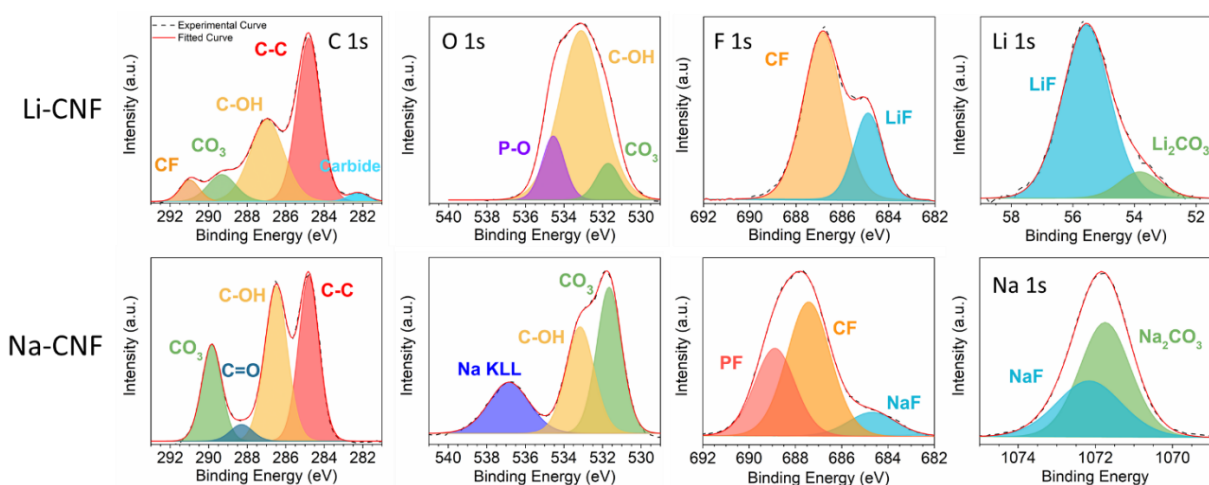


**Figure S3.7)** XPS after 3 mAh cm<sup>-2</sup> deposition for Li-CNF C1s, O1s, F1s, Li1s and Na-CNF C1s, O1s, F1s, and Na1s.

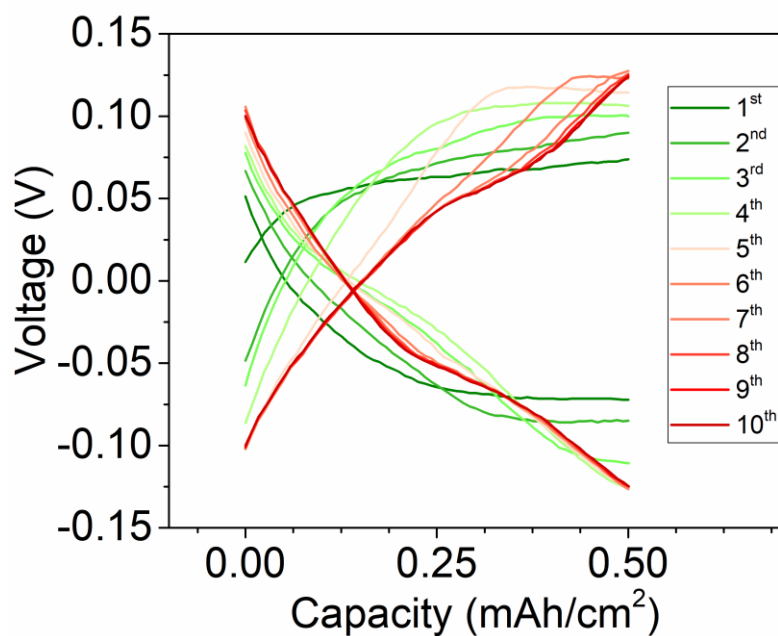


**Figure S3.8)** First ten cycles for Na-CNF||Na-CNF symmetric cell demonstrating the change in the cycling mechanism.

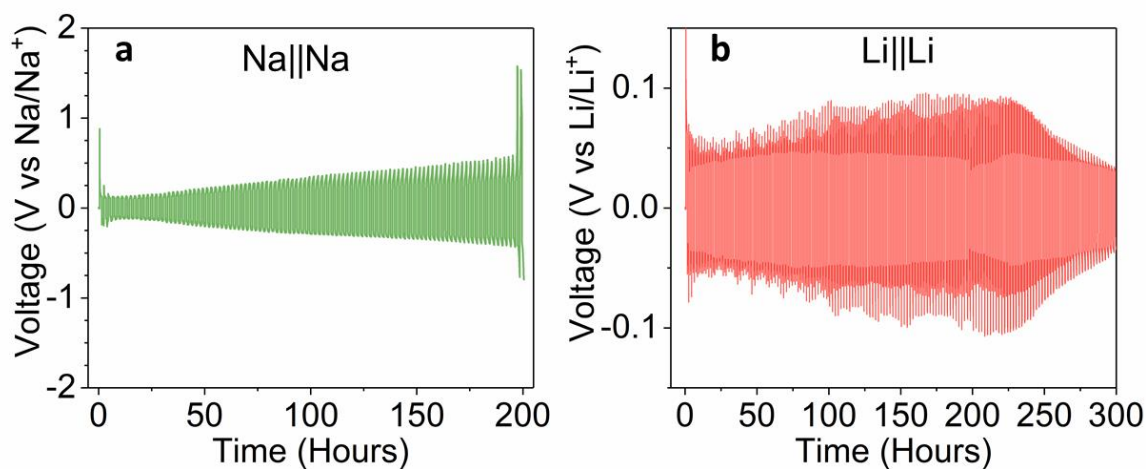


**Figure S3.9)** Cycling performance for a) sodium and b) lithium metal symmetric cells.

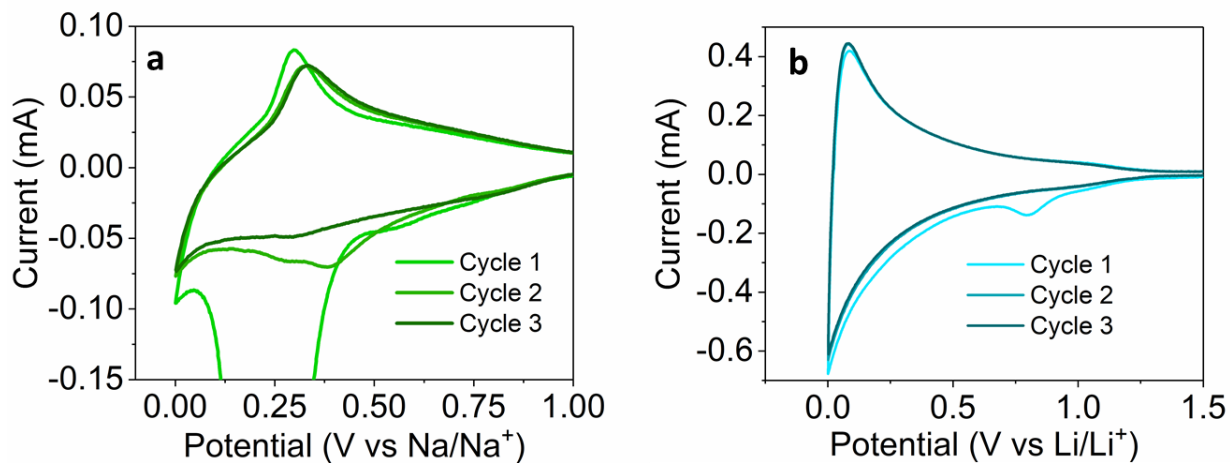


**Figure S3.10)** Zoomed in regions for a) Na||CNF and b) Li||CNF for CV cycling.

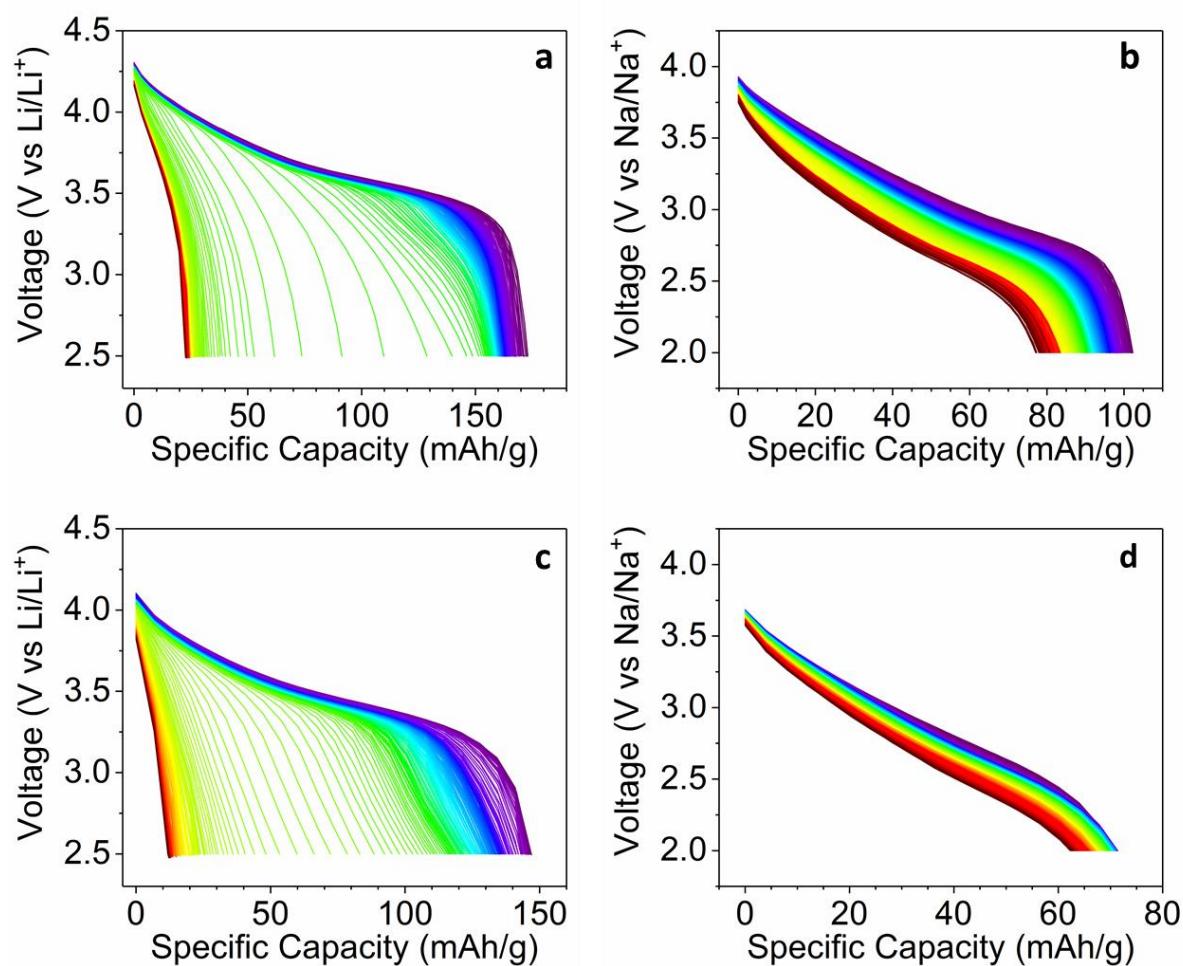


**Figure S3.11)** Galvanostatic discharge curves for NMC||Li-CNF and NFM||Na-CNF at 1C (a,b) and 2C (c,d).

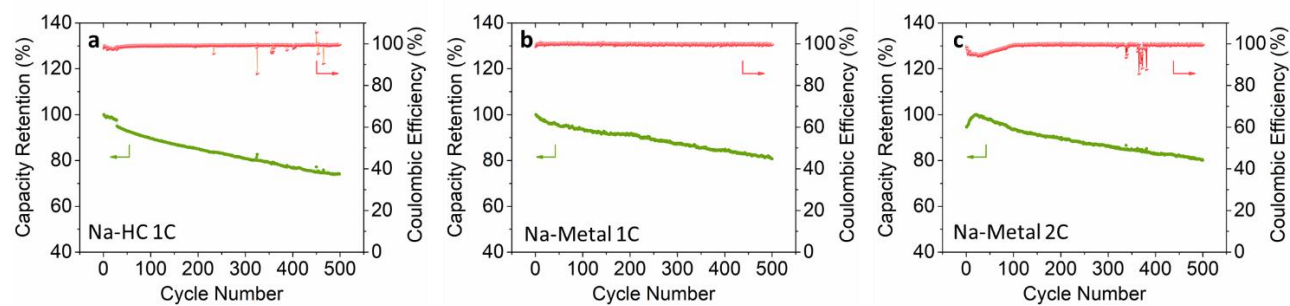


**Figure S3.12)** Capacity retention and CE plots for a) Na-HC at 1C, b) Na-Metal at 1C and c) Na-Metal at 2C full and half cells with the NFM333 cathode.

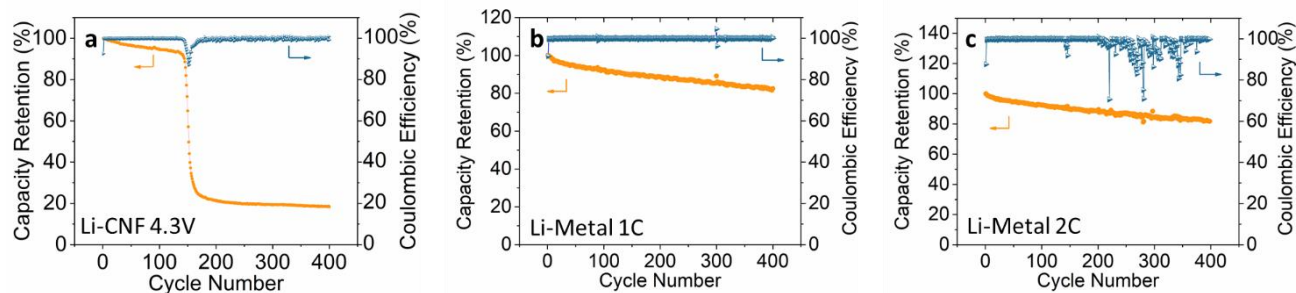


**Figure S3.13)** Capacity retention and CE plots for a) Li-CNF with an upper cutoff voltage of 4.3 V at 1C, b) Li-Metal at 1C and c) Li-Metal at 2C full and half cells with the NMC622 cathode.

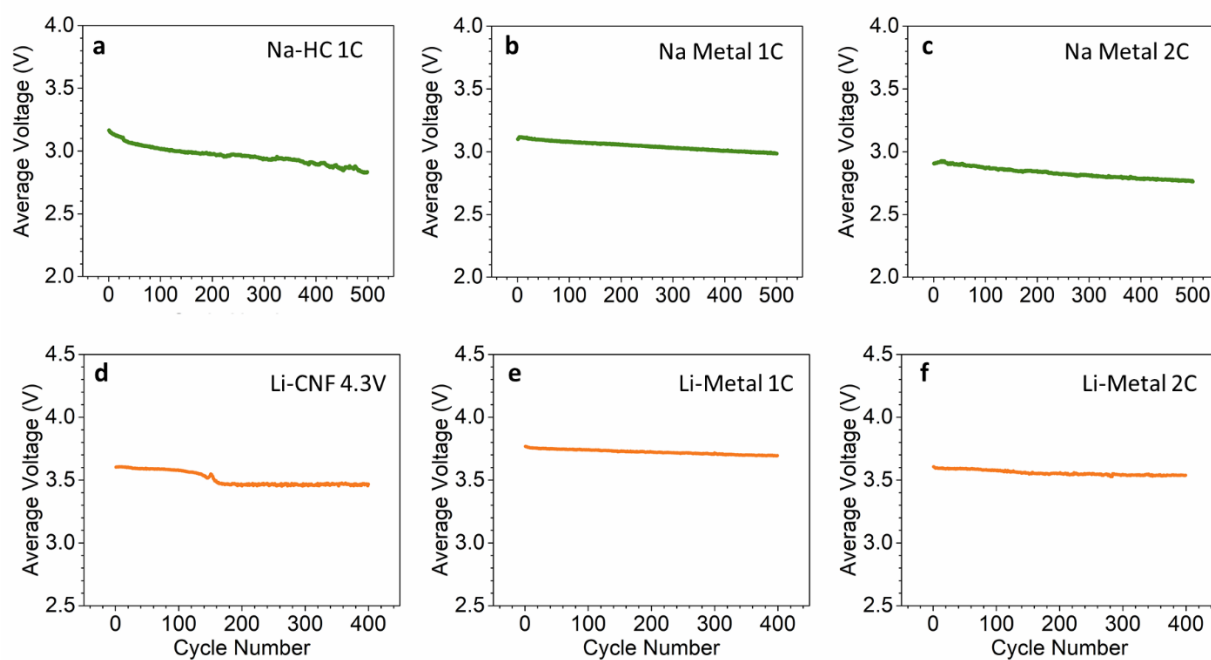


**Figure S3.14)** Average voltage profiles for Na- and Li- composite anode full cells and metal anode half cells.

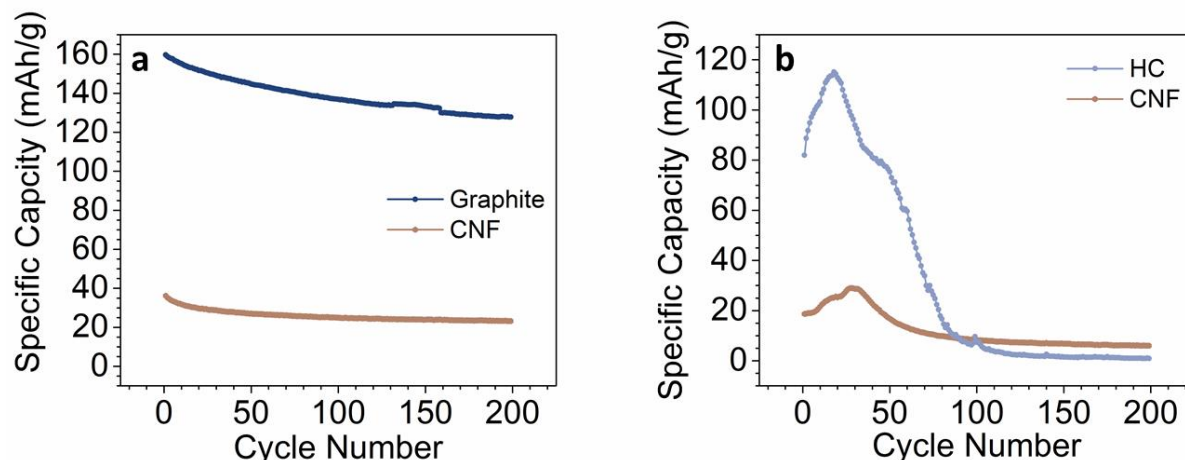


**Figure S3.15)** Full cell performance of a) NMC||Graphite and NMC||CNF and b) NFM||HC and NFM||CNF with pristine carbon anodes.

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## 4. Stabilizing the Cathode–Electrolyte Interfacial Chemistry through Electrolyte Engineering for Sodium Batteries

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### 4.1 Abstract

The increasing demand for alternative energy storage technologies has opened the avenue for sodium ion batteries to prosper for certain applications such as grid energy storage. Sodium ion battery commercialization has long been disregarded partially due to its inferior long-term stability, which is largely contributed by the poor electrode–electrolyte interfacial stability. This study brings forth an electrolyte formulation approach to enhancing the long-term stability of layered oxide cathode materials and develops a synchrotron-based experimental platform to investigate how the cathode–electrolyte interfacial chemistry impacts the cathode, separator, and anode in sodium cells. Through electrochemical diagnostics and electrolyte screening, we demonstrate that the inclusion of the sodium difluoro(oxolato)borate (NaDFOB) salt, in various electrolyte formulations, has shown great promise for cathode passivation and improving cycling stability. The NaDFOB salt can enable favorable cathode-electrolyte interfacial stabilization, which minimizes transition metal reduction and dissolution and mitigates mechanical damage of active particles. The systematic electrolyte screening establishes a complete understanding of the roles of individual salts and their combinations on the long-term stability of layered cathodes, leading to the development of several hero electrolyte formulations containing NaDFOB. In summary, the current study not only improves sodium electrode-electrolyte interfacial chemistry but also provides an experimental framework to characterize the interfacial processes and their electrochemical outcomes.

## 4.2 Introduction

Sodium ion batteries have been harboring more attention within the past decade as a potential alternative for large scale energy storage applications.<sup>1–4</sup> An attractive feature that sodium ion batteries benefit from is the potential to incorporate a wider variety of transition metals (TMs) in cathode materials, whereas practical lithium ion battery cathodes are currently limited to a few 3d TMs, including controversial cobalt. Therefore, sodium ion batteries can potentially be manufactured with low-cost, sustainable, earth-abundant elements to lower the final battery cost for wide scale implementation.<sup>5</sup> However, designing highly stable and high-capacity cathodes for such demanding applications is challenging due to their inferior practical capacity and structural stability.<sup>6–8</sup> Sodium layered oxides have been shown to be promising materials for sodium ion batteries due to their moderately high theoretical capacity, good electrochemical stability, and easy to scale synthetic methods.<sup>9</sup> Of the classifications for cathodes in sodium ion batteries, P2- and O3- type sodium layered oxides are regarded as the most promising cathode materials, which is reflected in the surging efforts reported in the literature. However, these materials can undergo multiple voltage plateaus during charging/discharging due to the formation of sodium vacancy ordered structures, leading to structural instability<sup>10</sup> Furthermore, the particle surface can become active for side reactions with the electrolyte, which is also an important cathode degradation mechanism.<sup>11–18</sup> Attempts have been made to suppress voltage plateaus and side reactions via surface coatings or pre-treatment of the sodium cathode in “cocktail” solutions before cycling.<sup>18</sup> Other attempts to improve cathode stability have been through engineering the electrolyte formulation.<sup>19,20</sup>

The compositions of the salt(s) and solvent(s) of the electrolyte largely affect the electrochemical and electrode–electrolyte interfacial reactions.<sup>21–25</sup> One of the most common

electrolyte formulations reported for sodium ion batteries is NaPF<sub>6</sub> dissolved in carbonate solvents such as propylene carbonate (PC). These electrolytes offer relatively high conductivity and wide electrochemical windows.<sup>19</sup> However, the PF<sub>6</sub> anion is well documented for producing HF as a decomposition product when reacting with trace amounts of water in the solvent and causing cathode degradation and TM dissolution.<sup>16,19,26–28</sup> Boron salt electrolytes have been shown over the past few decades to passivate cathode reactivity, prolong cycling stability, and reduce HF formation.<sup>29–34</sup> One of the most promising boron salt anions is difluoro(oxalato)borate (DFOB) for its highly stable cathode passivation properties, improved solubility in carbonate solvents, and the formation of a robust electrode–electrolyte interphase. The effects of LiDFOB as a single salt electrolyte, and as an electrolyte additive, have been heavily studied in lithium batteries.<sup>35–37</sup> In contrast, parallel efforts to study NaDFOB is sparse and has only recently begun to be investigated.<sup>38–40</sup> Some studies have reported that NaDFOB exhibits good solvent compatibility, stable Na||Na symmetric cycling, and favorable solid-electrolyte interphase (SEI) formation on sodium metal anode.<sup>38–40</sup> However, the impact of NaDFOB, either as the primary or auxiliary salt in the electrolyte, on the cathode performance has been largely unexplored. Previously, we investigated the underlying interfacial chemistry of the cathode–electrolyte interactions that dictate surface reconstruction, nanocrack formation, and transition metal dissolution on sodium layered oxide cathodes.<sup>11–15</sup> A complete understanding of how the electrolyte formulation may modulate the cathode surface chemistry can inform designing stable sodium batteries. Given the promising properties of the DFOB anion, we expect that including NaDFOB as part of the electrolyte salt can potentially provide a path towards stabilizing cathode–electrolyte interfacial chemistry and suppressing cathode degradation. Furthermore, when multiple Na salts are investigated through an electrolyte screening approach, we can expand the salt compositional space to develop a

comprehensive understanding of the roles of individual salts and their combinations on the battery performance. Last but not least, an experimental platform to characterize cathode–electrolyte interfacial processes can inform mechanistic understanding of the interplay between electrolyte composition and cathode chemical/structural stability.

Herein, we formulate a variety of sodium electrolyte compositions utilizing NaPF<sub>6</sub>, NaBF<sub>4</sub>, and NaDFOB in single, dual, and triple salt configurations and perform electrochemical analysis with the O3-NaNi<sub>1/3</sub>Fe<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> layered oxide cathode and study the cathode–electrolyte interfacial chemistries. We find that including NaDFOB salt in the electrolyte, as a primary, secondary, or tertiary salt, generally improves battery cycling stability. Through synchrotron spectroscopic and imaging techniques, we investigate the origin of the improved battery performance through the inclusion of NaDFOB at various temperatures. The decomposition byproducts of the DFOB anion forms a more robust cathode–electrolyte interphase (CEI), which protects cathode particles from continuous side reactions with the electrolyte and prevents excessive cathode particle degradation. We observe a suppression of transition metal reduction on the cathode surface, and mitigation of transition metal dissolution from the cathode onto the separator and sodium metal anode. This study demonstrates the importance of determining optimal synergistic pairings of electrolyte formulations in stabilizing the cathode–electrolyte interfacial chemistry for sodium batteries.

## 4.3 Results and Discussion

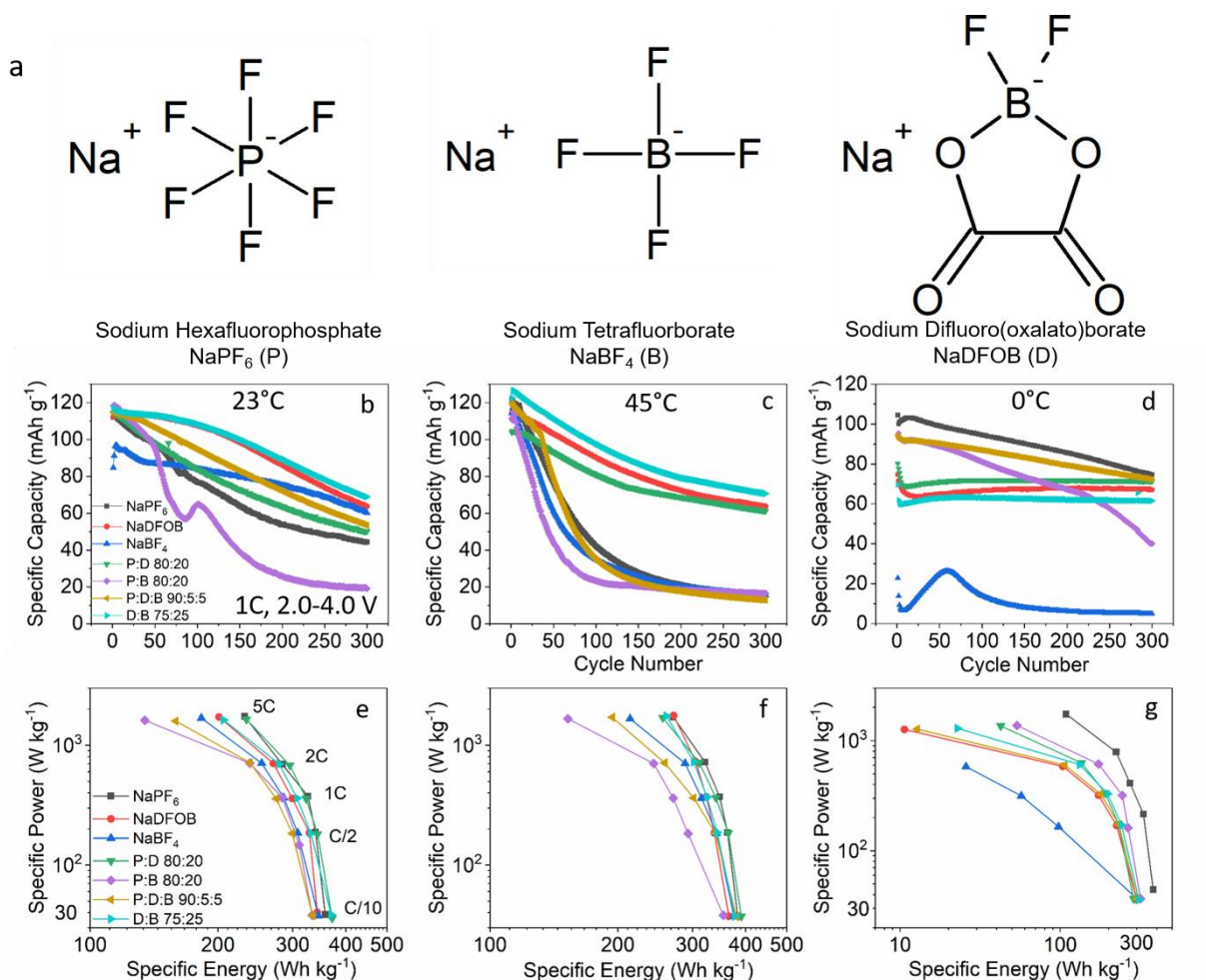


**Figure 4.1)** a) The chemical structures, names, and chemical formulas of the sodium salts used, with the abbreviated symbol in parentheses for combination naming scheme. Electrolyte electrochemical performance overview utilizing the O3-NaNi<sub>1/3</sub>Fe<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NFM 333) cathode and sodium metal anode at multiple temperatures. Discharge capacity, as a function of cycle number, at a rate of 1C in a voltage window of 2.0 – 4.0 V vs. Na/Na<sup>+</sup> at b) 23°C, c) 45°C, and d) 0°C. Ragone plots derived from the average discharge capacity of 5 cycles from rate capability testing (Figure S4.2) at different C-rates cycled at e) 23°C, f) 45°C, and g) 0°C.

### 4.3.1 Electrochemical performance of electrolyte mixtures

The O3-NaNi<sub>1/3</sub>Fe<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cathode is paired with sodium metal foil anode for the performance measurements throughout the breadth of this study. The three main sodium salts used throughout this study are NaPF<sub>6</sub>, NaBF<sub>4</sub>, and NaDFOB (Figure 4.1a) at 1M total concentration dissolved in a propylene carbonate (PC) solvent. In the first part of this section, we aim to use

electrochemical measurements to down-select representative electrolyte compositions for further investigation. We achieve this through changing the salt ratio in the PC solvent. The fraction for the secondary salt is tailored around 2%-25% to observe the effect of electrolyte compositions on battery performance.

The electrochemical measurements for all electrolyte combinations are performed over 300 cycles at a current rate of 1C, operating voltage window between 2.0 – 4.0 V, and 23 °C (Figure S1a-e). Figure 4.1b shows a smaller set of electrolyte compositions selected from Figure S4.1. Of the three pure salt electrolytes NaPF<sub>6</sub> provides high initial specific discharge capacity (~115 mAh g<sup>-1</sup>) but poor capacity retention (39.5%) (Figure 4.1b and Figure S4.1a). NaBF<sub>4</sub> continuously provides low initial specific discharge capacity ~90 mAh g<sup>-1</sup> yet the best cycling stability at 62.2% (Figure 4.1b and Figure S4.1a). NaDFOB provides the overall best cycling performance with an initial specific capacity ~115 mAh g<sup>-1</sup> and capacity retention in between NaPF<sub>6</sub> and NaBF<sub>4</sub> (54.9%) (Figure 4.1b and Figure S4.1a).

We then perform battery measurements using NaPF<sub>6</sub> as the main salt to determine the effect of sodium boron salts as secondary salts on cycling stability. The inclusion of NaDFOB to the NaPF<sub>6</sub> electrolyte generally has shown an improvement in cycling stability relative to the pure NaPF<sub>6</sub> electrolyte (Figure S4.1b). All the P:B series, i.e., adding NaBF<sub>4</sub> to NaPF<sub>6</sub>, perform noticeably worse than pure NaPF<sub>6</sub> (Figure S4.1c), which suggests that NaBF<sub>4</sub> is not a good secondary salt to the NaPF<sub>6</sub> electrolyte, although NaBF<sub>4</sub> provides reasonable performance as a pure salt (Figure 4.1b). When both NaDFOB and NaBF<sub>4</sub> are implemented as secondary salts to NaPF<sub>6</sub> in the P:D:B series (Figure 4.1b and Figure S4.1d), the detrimental effects of the NaBF<sub>4</sub> at a higher concentration (10%) overtake the beneficial effect of the NaDFOB and lowers the cycling stability of the Na cell (Figure S4.1d).

Next, we combine NaDFOB and NaBF<sub>4</sub> salts together, as the combination of LiBF<sub>4</sub> and LiDFOB has been reported to improve the cycle life of Li cells.<sup>41</sup> We mix NaDFOB and NaBF<sub>4</sub> together in ratios of 25:75, 50:50, and 75:25 (D:B) to determine which boron salt works better as the main salt and the other as the secondary salt (Figure S4.1e). All combinations work better than pure NaPF<sub>6</sub>, and D:B 75:25 is shown to have better performance than other D:B compositions (Figure S4.1e). As the DFOB anion undergoes electrochemical decomposition, NaBF<sub>4</sub> can be formed as a side product and can continue to cycle with high stability similar to the pure NaBF<sub>4</sub> salt electrolyte in Figure 4.1b, improving overall cycling longevity.<sup>41</sup> Based on the electrochemical measurements of many electrolyte compositions, we down-select the compositions that typically show the highest cycling stability over the 300 cycles, with the exception of the P:B series where the worst performing mixture (i.e., P:B 80:20) is selected. P:B 80:20 is selected to better understand the effect of the NaBF<sub>4</sub> as a secondary salt on the performance of NaPF<sub>6</sub> in Na cells. These down-selected electrolyte compositions are highlighted in red boxes in Figure S4.1f and presented in Figure 4.1b. We then perform electrochemical measurements of these down-selected electrolyte compositions at 45°C and 0°C.

The temperature is increased to 45°C to test the cycling stability of the electrolytes under more thermally demanding conditions (Figure 4.1c). Boron based electrolytes have been shown to have improved performance and stability at higher temperatures, compared to Li- or NaPF<sub>6</sub>.<sup>29,42,43</sup> Over the 300 cycles, an obvious difference in cell stability is observed for the electrolytes that contain higher amounts of NaDFOB (Figure 4.1c), with pure DFOB, P:D 80:20, and D:B 75:25 having better capacity retention at the elevated temperature than that at room temperature. The improved thermal performance is partially due to the enhanced ionic kinetics and increased conductivity of the electrolytes at elevated temperatures and the better thermal stability of the

DFOB salt.<sup>42,44</sup> The DFOB salt also produces a more stable and robust CEI through the ring opening decomposition pathway of the DFOB anion, which undergoes an oligomerization process that forms a strong oligomer network in the CEI and protects cathode particles from continuous side reactions with the electrolyte.<sup>34,40,45</sup> On the other hand, when cycled at 0°C, the boron containing electrolytes have a poorer initial capacity, especially those containing higher amounts of the bulky DFOB anion (Figure 4.1d). Compared to the cycling performance at 45°C and 23°C, the cell with the pure NaPF<sub>6</sub> electrolyte has a minor decrease in its discharge capacity and a reduced rate of capacity fading. The cell with the pure NaBF<sub>4</sub> electrolyte is practically unable to cycle due to the decreased salt solubility and conductivity at lower temperatures. While the cells with a higher concentration of NaDFOB, either as the primary or secondary salt, have a much lower initial capacity (60-80 mAh g<sup>-1</sup>) and their cycling stability is improved, with no visible decrease in capacity over the 300 cycles. In summary, the electrochemical measurements at 45°C and 0°C led to these conclusions: NaDFOB is more thermally stable than NaPF<sub>6</sub> and improves the overall cycling performance at higher temperatures. At lower temperatures, the inclusion of NaDFOB greatly improves cell stability but lowers the cell capacity due to having lower ionic mobility and salt solubility. Next, we evaluate the rate capability of the cells containing different down-selected electrolytes.

Rate capability of these cells are measured at the same temperature ranges as the long-term cycling, going through the current rates from C/10 increasing to 5C and returning to C/10 (Figure S4.2). Starting at 23°C, at rate of 5C the Na cells containing NaBF<sub>4</sub>, P:B, and P:D:B electrolytes delivered a 61%, 49%, 55% of the capacity at C/10, respectively. The rate capability of the Na cells containing NaDFOB and D:B electrolytes delivered 68% and 65%, respectively, with NaPF<sub>6</sub> having the highest rate capability at 73% (Figure S4.2a). The cells containing NaDFOB as the

primary or secondary salt maintain a higher cycling stability throughout the rate capability measurement (Figure S4.2). We calculate the capacity retentions of the rate capability measurements from the average of the initial and final 5 cycles at the C/10 rate (Table S1, ). While the electrolytes that have better ionic mobility allow for a better rate capability, they may not have the most stable cycling performance. For example, the NaPF<sub>6</sub> electrolyte provides a good rate capability but has poor cycling stability (Figure S4.2, Table S4.1)

We then measure the rate capability at 45°C. All the electrolyte compositions have improved rate capability at the elevated temperature. The Na cells cycled with NaDFOB and D:B 75:25 have an improved rate capability of 78% and 74%, respectively, reaching near, or surpassing, the rate capability provided by the NaPF<sub>6</sub> electrolyte (76%) (Figure S4.2b). The NaPF<sub>6</sub> cell's cycling stability decreases more significantly than the NaDFOB and D:B electrolytes (Figure S4.2b). The P:D 80:20 electrolyte also shows an improved stability in capacity retention from the inclusion of NaDFOB (Figure S4.2b). The rate capability at 0°C mirrored the long-term cycling performance with the boron containing electrolytes having a significantly worse discharge capacity and rate capability. However, all electrolytes have improved stability, maintaining above 95% capacity retention when returning to the C/10 rate (Figure S4.2c, Table S4.1).

We next measure the effect of the electrolyte formulation on the specific energy and power output of the NFM 333 cathode in the Na cell using Ragone plots. The Ragone plots are calculated from the average of the 5 cycles per C rate from the rate capability testing (Figures 4.1d-f and Figure S4.2). At 23°C the NaPF<sub>6</sub> and P:D 80:20 electrolytes maintained the highest specific energy (~230 Wh kg<sup>-1</sup>) at 5C, followed by NaDFOB and D:B 75:25 overlapping each other ~200 Wh kg<sup>-1</sup> and the NaBF<sub>4</sub>, P:B, P:D:B electrolytes having the lowest specific energy (130-180 Wh kg<sup>-1</sup>) (Figure 4.1e). When we increase the cycling conditions to 45°C, the performance for the NaDFOB

containing electrolytes is improved, with the NaDFOB and D:B cells almost overlapping with NaPF<sub>6</sub> cell at the higher C-rates. When lowering the temperature to 0°C, the specific power and specific energy of the boron electrolytes is significantly hampered from the slower kinetics from ionic limitations, especially for NaBF<sub>4</sub> which was unable to cycle properly at 5C.

In summary, while NaPF<sub>6</sub> typically provides the best initial discharge capacity it suffered from severe capacity fading at 23°C and accelerated deterioration at 45°C, yet maintained its high capacity and an enhanced stability at 0°C. The use case for NaPF<sub>6</sub> may be desirable for applications that require a higher power output with a short cycle life or in lower temperatures, but the cycling instability at room or elevated temperatures may cause many challenges for long-term applications. Meanwhile, the utilization of NaDFOB as a primary or secondary salt improves the cycling stability in nearly every electrolyte composition at all temperature ranges, and the cells maintain a competitive practical capacity at room and elevated temperatures. For the remainder of this study, we further down-select the representative electrolytes in the main text to the NaPF<sub>6</sub>, NaBF<sub>4</sub>, NaDFOB, and D:B 75:25 electrolytes, with the P:D, P:B, and P:D:B data presented in the . Our aim is to investigate the cathode–electrolyte interfacial chemistry as a function of electrolyte formulation, with a focus on comparing the pure salt electrolytes with the overall best performing mixed-salt electrolyte (D:B 75:25) in the main text.

### 4.3.2 Probing the cathode–electrolyte interfacial chemistry

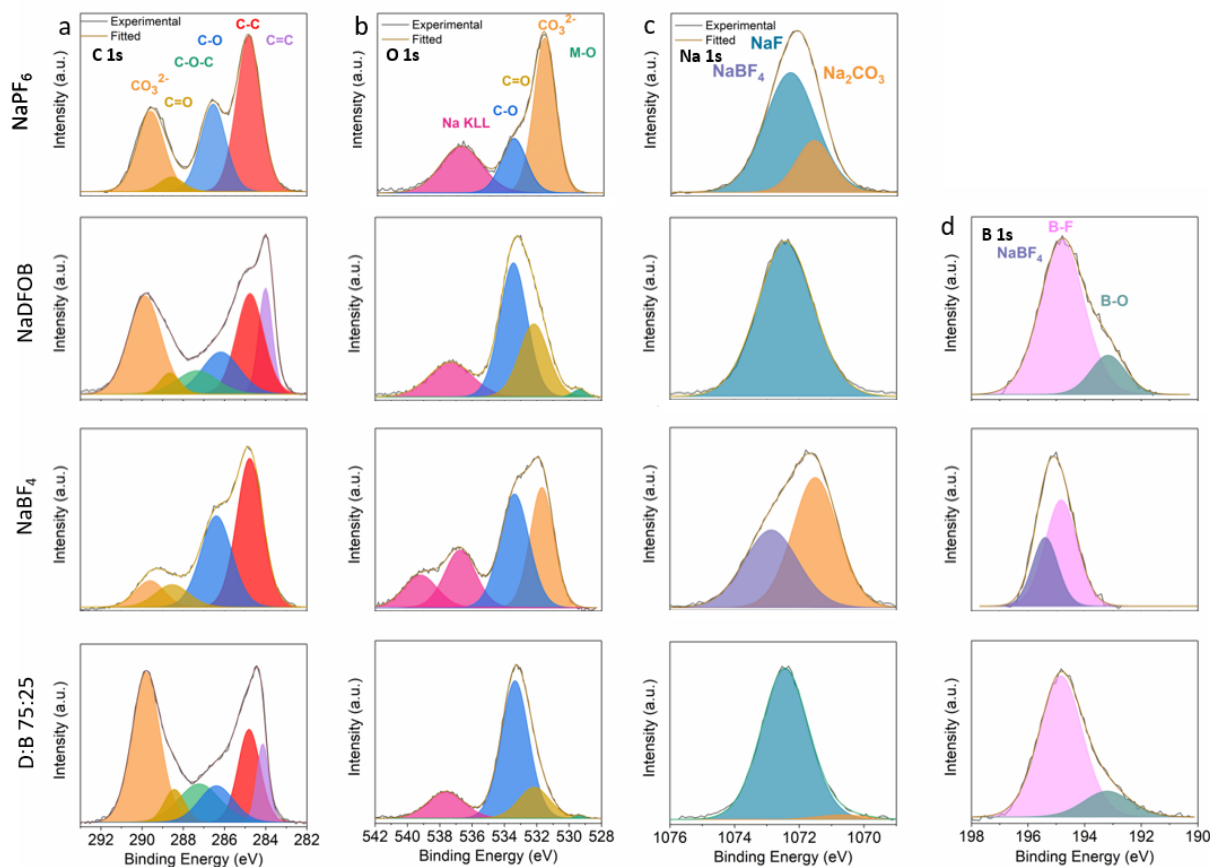


**Figure 4.2)** XPS characterization of the cycled NFM 333 cathode surface cycled with NaPF<sub>6</sub>, NaDFOB, NaBF<sub>4</sub>, and D:B 75:25 electrolytes after 300 cycles at 23°C. a) C 1s, b) O 1s, c) B 1s, and d) B 1s XPS spectra.

The interfacial reactions between the cathode and the electrolyte are one of the main factors that govern the overall cathode stability and lifespan of the Na cell.<sup>31,46,47</sup> In this section, we use multiple diagnostic techniques to investigate the composition and stability of the CEI. X-ray photoelectron spectroscopy (XPS) is used to investigate the byproducts of the cathode–electrolyte interfacial reactions on the cathode surface and determine the chemical composition of the CEI after 300 cycles at 23°C (Figure 4.2 and Figure S4.3). In the C 1s spectra, after cycling, we observe peak formation for C=C and C-O-C species only in the CEI of the cathodes that were cycled with NaDFOB containing electrolytes (Figure 4.2a and Figure S4.3a). The C=C and C-O-C peaks, and

strong  $\text{CO}_3^{2-}$  peaks correspond to byproducts formed during the ring opening and oligomerization mechanism of the electrochemical degradation of the DFOB anion.<sup>34,40,45</sup> The P:D and P:D:B electrolytes also show strong peak intensity for the C=C and C-O-C species (Figure S4.3a). Therefore, even at lower concentrations, the oligomerization of the DFOB anion can modify the CEI composition and improve the overall cycling stability of NFM333.

A unique M-O peak is observed in the O 1s spectra for the cycled NaDFOB-containing electrolytes (Figure 4.2b). The presence of this peak hints that the CEI produced from the NaDFOB decomposition is either 1) thin enough that the NFM cathode surface is able to be probed, detecting the TM-O lattice oxygen<sup>48</sup>, or 2) that the NaDFOB decomposition products can chemically bond with transition metal cations that migrate from the cathode surface.<sup>49</sup> The inability to detect an M-O peak on the cathodes with  $\text{NaPF}_6$  and  $\text{NaBF}_4$  electrolytes could infer the formation of a thicker CEI due to a higher degree of electrolyte degradation. For the cathodes cycled in the NaDFOB-containing electrolytes, the  $\text{Na}_2\text{CO}_3$  peak is significantly reduced in the Na 1s spectra (Figure 4.2c). Instead, these electrodes show strong peaks for NaF formation. Meanwhile, for the  $\text{NaPF}_6$  containing electrolytes, strong  $\text{Na}_2\text{CO}_3$  peaks suggest the formation from the continuous decomposition of  $\text{NaPF}_6$  (Figure 4.2c and Figure S4.3c). Lastly, the B 1s spectra for all boron containing electrolytes show similar results with a strong B-F peak, and less intense B-O peak, with the exception of the pure  $\text{NaBF}_4$  electrolyte cathode (Figure 4.2d and Figure S4.3d). The Na 1s and B 1s for  $\text{NaBF}_4$  both have a strong peak for  $\text{NaBF}_4$  that suggests that the  $\text{NaBF}_4$  salt is resilient to electrochemical degradation and deposits on the cathode surface. Byproducts of NaDFOB decomposition can lead to the formation of  $\text{BF}_4$  and  $\text{B}_2\text{O}_5$  species, with the borate formation also contributing to improved structural stability of the CEI.<sup>38,41</sup> Overall, the decomposition products of the DFOB anion potentially plays a significant role in improving

cathode stability via the ring opening and oligomerization mechanisms. As a result, a robust passivation layer is formed to prevent further cathode–electrolyte side reactions that would further degrade cathode structure and stability.

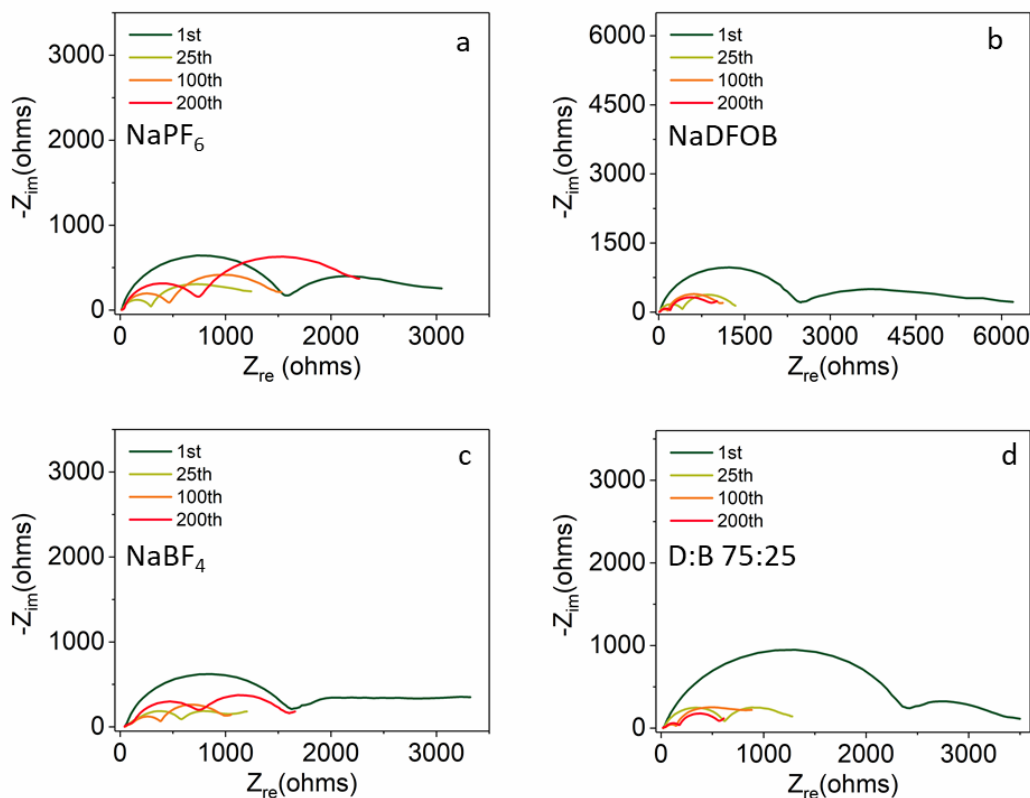


**Figure 4.3)** Electrochemical impedance spectroscopy (EIS) of the Na cells after the 1<sup>st</sup>, 25<sup>th</sup>, 100<sup>th</sup>, and 200<sup>th</sup> cell cycles at 23°C for a) NaPF<sub>6</sub>, b) NaDFOB, c) NaBF<sub>4</sub>, and d) D:B 75:25 electrolytes.

We then measure the electrochemical impedance spectroscopy (EIS) of the cells to observe the stability electrode-electrolyte interphase in the Na cell after 1, 25, 100, and 200 cycles at 23°C (Figure 4.3 and Figure S4.4). For all the spectra, we observe two semi-circles: one at a higher frequency (left semi-circle) that is associated with the resistance at the electrode-electrolyte interface and the right semi-circle which is related to charge-transfer resistance.<sup>50</sup> By measuring

the changes in the semi-circle shape of the Na cell, over increasing cycle number, we can obtain insight into the effective stability of the electrode-electrolyte interphase of the Na cell.

After the first cycle, the radius of the first semi-circle is larger for the cells cycled with NaDFOB and D:B electrolytes when compared to those with the pure NaPF<sub>6</sub> and NaBF<sub>4</sub> electrolytes (Figure 4.3a-d). The initial formation stages of the CEI for the NaDFOB containing electrolytes has a higher electrode-electrolyte resistance, with the pure NaDFOB CEI also having a higher charge-transfer resistance (Figure 4.3 and Figure S4.4). We also observe that the semi-circle related to the electrode-electrolyte interface P:D, P:B, and P:D:B electrolytes are larger than the Na cells with pure NaPF<sub>6</sub> or NaBF<sub>4</sub> electrolytes, suggesting an initial incompatibility during the CEI formation from the decomposition of the multiple sodium salts in the electrolyte (Figure S4.4a-c). The radius of both semi-circles gradually decreases for all electrolyte compositions after 25 cycles as the CEI “optimizes” itself during subsequent cycles, suggesting a decrease in the resistances related to the electrode-electrolyte interface and charge-transfer.<sup>51</sup> The semi-circles for the cells cycled with the NaDFOB containing electrolytes continued to decrease over the 200 cycles, with the exception of P:D starting to increase after 200 cycles (Figure 4.3b,d and Figure S4.4a,c). On the other hand, after 100 cycles, both semi-circles for the NaPF<sub>6</sub>, NaBF<sub>4</sub>, and P:B electrolytes increased (Figure 4.3a,c and Figure S4.4b). Through having small stable electrode-electrolyte interfacial resistance, the CEI allows for improved electrochemical performance in the cells over long-term cycling. The lack of a stable CEI is unable to effectively passivate the cathode surface from continuous side reactions and gradually increases the cell’s internal resistance over time. The results from EIS are consistent with the CEI composition information obtained from the XPS analysis in Figure 4.2 and electrochemical performance in Figure 4.1. The CEI formed from

the decomposition of the DFOB anion leads to a highly optimized passivation layer and reduces the overall cathode-electrolyte resistance for improved long-term cycling.

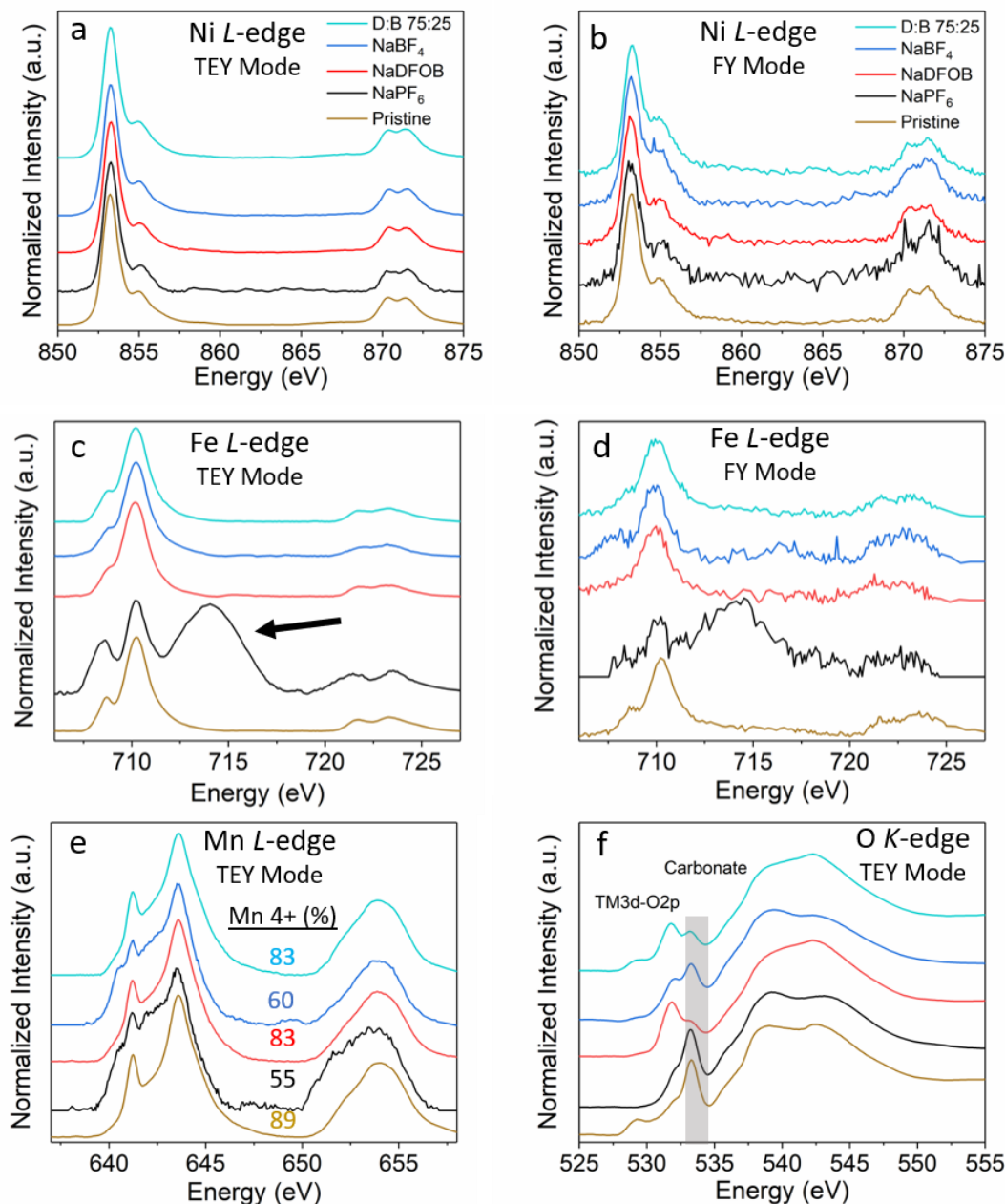


**Figure 4.4)** Interfacial chemistry analysis using soft X-ray absorption spectra of the NFM333 cathode at pristine condition and after 300 cycles with the NaPF<sub>6</sub>, NaDFOB, NaBF<sub>4</sub>, and D:B 75:25 electrolytes in the discharged state for Ni a) TEY and b) FY modes, Fe c) TEY and d) FY modes, e) Mn TEY mode L-edges and f) O K-edge TEY mode. The included arrow in Fig. 4c pointing at the large hump present only in the spectra of NaPF<sub>6</sub> electrolytes and grey area in Fig. 4f highlighting the peak for carbonate species in the O K-edge spectra.

For the Mn L-edge spectra, in the TEY mode, we performed linear combination to calculate the approximate relative percentages of  $\text{Mn}^{2+}$  –  $\text{Mn}^{4+}$  oxidation states in each sample (Table S4.2). The pristine sample was primarily in the  $\text{Mn}^{4+}$  state. The  $\text{NaPF}_6$  and  $\text{NaBF}_4$  cycled electrodes have a higher degree of Mn reduction and the NaDFOB and D:B 75:25 electrolytes retain a near-pristine oxidation state (Figure 4.4e). Higher degrees of TM reduction can increase the rate of TM dissolution from the cathode particles and cause structural instability in the cathode lattice structure.<sup>16,54–57</sup> The inclusion of the NaDFOB as a secondary salt in the P:D 80:20 electrolyte also had enhanced stability and was able to mitigate the degree of Mn reduction compared to the pure  $\text{NaPF}_6$  cycled cathode.<sup>45</sup> Meanwhile, the addition of  $\text{NaBF}_4$  as a secondary salt exacerbated Mn reduction (Figure S4.5e). Qualitative information on the CEI thickness and presence of carbonate species on the surface of the cycled electrodes can be gained from the O K-edge. The spectra of the TEY mode shows that the samples cycled with the pure  $\text{NaPF}_6$  and  $\text{NaBF}_4$  electrolytes have a stronger peak intensity for carbonate species than those cycled with NaDFOB containing electrolytes (Figure 4.4f and Figure 4.5f). The samples cycled with the NaDFOB containing electrolytes also show stronger intensities for the TM3d-O2p hybridized states, suggesting that we were able to probe part of the cathode particles. The O K-edge spectra suggests that cathodes cycled with the NaDFOB containing electrolytes produced a more compact CEI, that also contain a smaller amount of  $\text{Na}_2\text{CO}_3$  on the cathode surface, corresponding with the O 1s and Na 1s XPS results discussed in section 4.3.2. As we probe the subsurface, in the O K-edge FY mode, the carbonate species peak intensity is reduced and the TM-O hybridization peak intensity increased on the cathode for nearly all the electrolyte compositions, with the exception of the  $\text{NaBF}_4$  and P:B samples which maintains a strong carbonate peak (Figure S4.6). The results suggest that the  $\text{NaBF}_4$  and P:B cycled electrodes have a thicker CEI, which would correspond with the large growth in

impedance shown in Figure 4.3 and Figure S4.4. From the performance data and characterization measurements taken so far there appears to be an incompatibility between the NaPF<sub>6</sub> and NaBF<sub>4</sub> salts, leading for the formation of a thick and unstable CEI, which is incapable of protecting the cathode from continuous side reactions and particle degradation. The XAS measurements reveals that the P:B 80:20 cycled samples has the highest amount of TM reduction for both Fe and Mn over the multiple XAS measurements.

In summary, the O K-edge spectra indicate the formation of a compact CEI on the cathode cycled with the NaDFOB containing electrolytes, which protects the cathode from continuous interfacial degradation and improves the cycle life of Na cells. Indeed, the soft XAS Ni, Fe, and Mn spectra reveal that the cathodes cycled with the NaDFOB containing electrolytes suppressed TM reduction in the surface and subsurface of cathode particles.

With how severe the reduction of Fe had leached into the subsurface of the cathode, in the sXAS FY mode (Figure 4.4d), we then probe the bulk structure of the NFM cathode with synchrotron hard X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) to ascertain the bulk oxidation states and local structural environment, respectively (Figure 4.5 and Figure S4.7). While the Ni L-edge showed no significant change in the oxidation state at the surface of the cathode (Figure 4.4a), the Ni K-edge, however, reveals that the Ni in the bulk of the cathode is oxidized for all of the cycled cathode electrolytes, due to the loss of Na ions from the cathode lattice (Figure 4.5a and Figure S4.7a).<sup>11,13</sup> Although the concentration of Na ions decreases in the cathode over time, it does not directly correlate to fade in capacity, as NaDFOB and D:B 75:25 has some of the highest capacity retention results, yet had the highest degree of Ni oxidation in the bulk. The Fe K-edge shows that cathode cycled with pure NaPF<sub>6</sub> is the only electrolyte that reduced Fe in the bulk structure (Figure 4.5b).

However, all NaPF<sub>6</sub> containing electrolytes cause higher degrees of Mn reduction, than those do not contain NaPF<sub>6</sub> (Figure 4.5c and Figure S4.7c). These results of the bulk structure coincide with the greater degree of reduction found on the surface and subsurface from sXAS with NaPF<sub>6</sub> containing electrolytes (Figure 4.4).

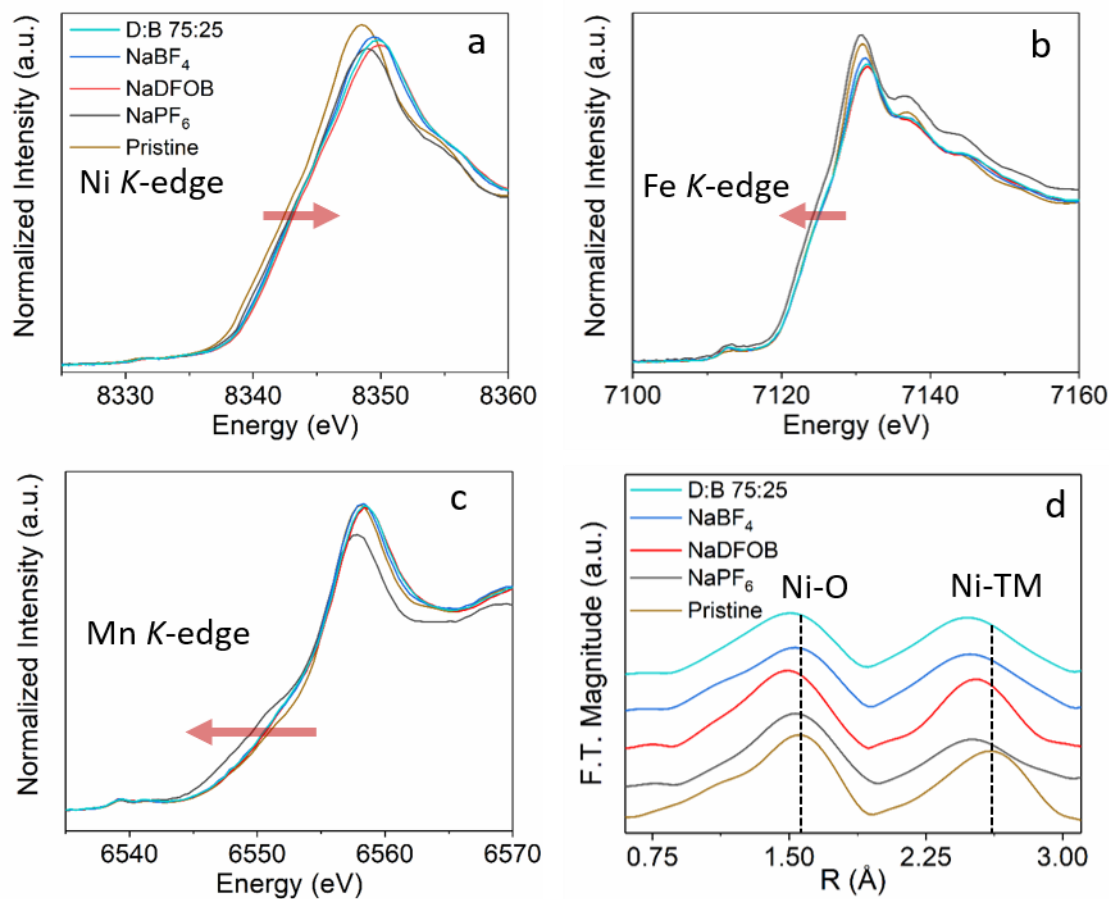


**Figure 4.5)** Oxidation-state evolution of the transition metals using hard X-ray absorption near edge structure (XANES) spectra the a) Ni K-edge, b) Fe K-edge, and c) Mn K-edge of the NFM333 cathode at the pristine state and after 300 cycles with the NaPF<sub>6</sub>, NaDFOB, NaBF<sub>4</sub>, and D:B 75:25 electrolytes in the discharged state. The arrows indicate the oxidation state shift from the pristine state after cycling. Fourier-transformed extended X-ray absorption fine structure (EXAFS) for d) Ni after cycling, where the dashed lines show the peak positions for the pristine sample.

The Ni EXAFS shows reduction in the Ni-O and Ni-TM bond lengths as a result of Na loss in the lattice and contributed to a small percentage of volume change in the cathode lattice.<sup>11</sup> The X-ray diffraction (XRD) patterns of the pristine and cycled electrodes show that some of the electrodes have some irreversible changes from the O3/P3 phase transformation and minor peak shifts after long-term cycling (Figure S4.8).<sup>58</sup> The cathode cycled with the D:B 75:25 electrolyte maintains a higher degree of structural stability, with minimal peak shift in its XRD pattern compared to the pristine electrode.

In summary, Fe is shown to be the most reactive TM present in the cathode and easily undergoes TM reduction, dissolution, and, potentially, redeposition to the cathode surface. The inclusion of the NaDFOB salt successfully helps to suppress excessive cathode-electrolyte side reactions and maintains a stable local chemical environment for the cathode. The CEI formed from the NaDFOB anion byproducts protects the cathode TMs from a higher degree of reduction over long-term cycling on the surface and in the bulk.

#### **4.3.3 Quantifying transition metal dissolution**

The instability of the oxidation state in the surface and bulk of the cathode particles has contributed to performance loss, surface reconstruction, and transition metal dissolution. We investigate the transition metal dissolution and deposition on to the Na metal anode through synchrotron X-ray fluorescence microscopy (XFM) after long-term cycling (Figure 4.6). The NaPF<sub>6</sub> electrolyte has the highest degree of TM reduction on the surface and in the bulk of the NFM cathode and is also found to result in the most extensive Fe, Mn, and Ni deposition on the anode surface (Figure 4.6a-c). Of all the TMs, Fe has the highest concentration on the Na metal anode, for all electrolytes (Figure 4.6a-c and Table S4.3). The Fe cation concentration for anode cycled with pure NaPF<sub>6</sub> is 621 times the concentration measured on the D:B 75:25 anode. The

anode cycled with D:B 75:25 has the lowest concentration of deposition of all TMs cations. Photographs of the separators after the 300 cycles at 23°C, facing the cathode side of the Na cell, are shown in Figures 4.6d-g and Figure S4.9. The separator of the PF<sub>6</sub>-containing cell has the highest degree of discoloration from the pristine white color to a yellow-brown color in the center of the separator and black around the edges (Figure 4.6d). The separators for all boron electrolytes, with the exception of P:B 80:20, maintain a near pristine white color.

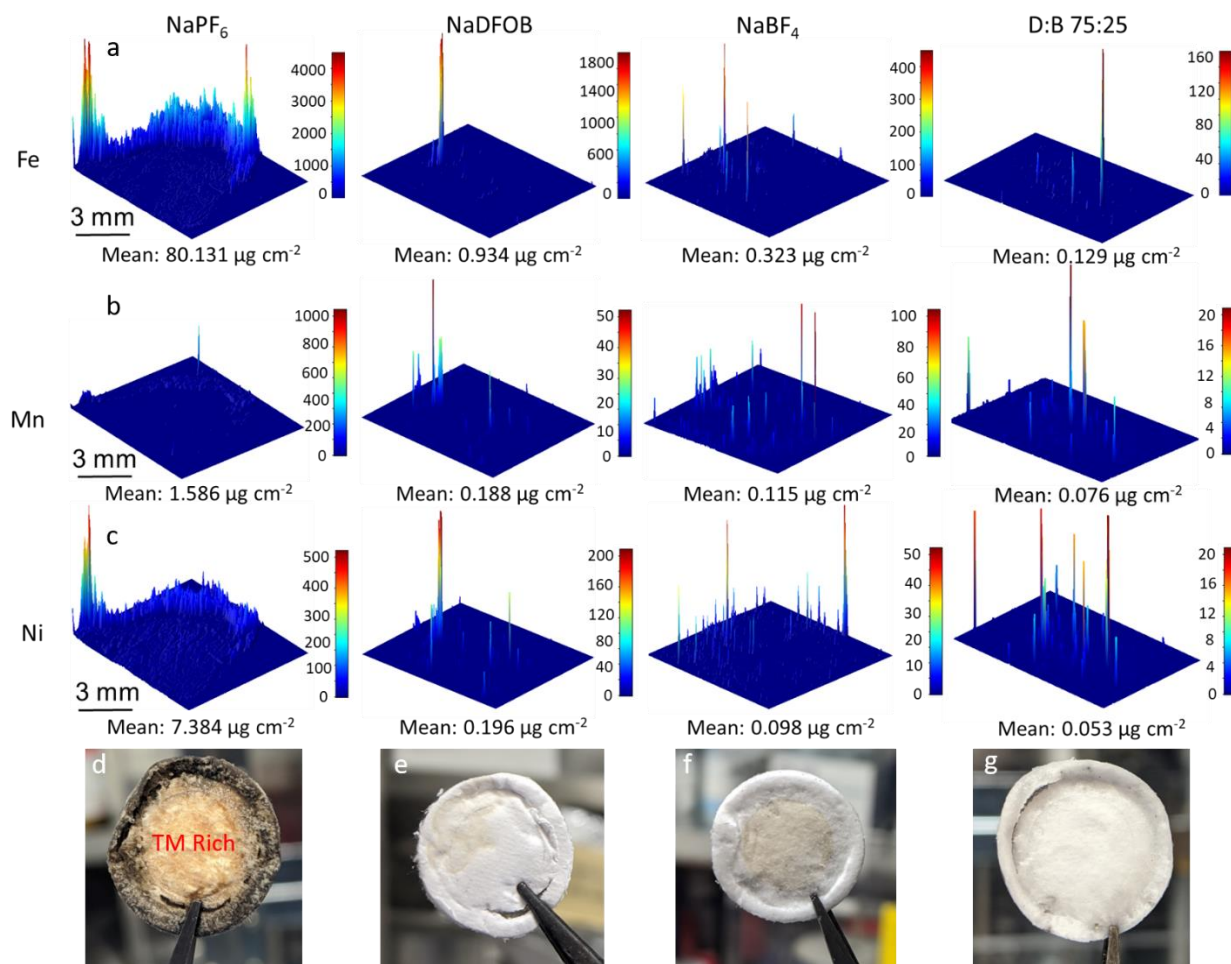


**Figure 4.6)** Quantification and distribution of transition metals deposited on the cycled sodium metal anode after 300 cycles at 23°C at a 1C rate utilizing synchrotron x-ray fluorescence microscopy of a) Fe deposition, b) Mn deposition, c) Ni deposition cycled with NaPF<sub>6</sub>, NaDFOB, NaBF<sub>4</sub>, and D:B 75:25 electrolytes, respectively. The color bar shows the corresponding concentrations ( $\mu\text{g cm}^{-2}$ ) of the elements on Na anode at a particular color. Photographs of separators, facing the cathode side after cycling, highlighting the change in color from TM dissolution for d) NaPF<sub>6</sub>, e) NaDFOB, f) NaBF<sub>4</sub>, and g) D:B 75:25 electrolytes.

In addition to the XFM analysis, we use ICP-MS on the separator to further quantify the concentration of TM deposition (Table S4.4). Overall, the measured ICP-MS results of the separator is consistent with the XFM analysis on the Na metal anode, with Fe having the highest concentration of TM dissolution in the Na cell. The ICP-MS results for the P:B 80:20 cell also has the highest concentration for all TMs, followed by the NaPF<sub>6</sub> cell having second highest concentration, and the pure NaBF<sub>4</sub> and all NaDFOB containing cells significantly reducing the concentration of TM dissolution for all metals. As reported in other works, Fe also had the highest degree of TM dissolution found on the Na metal anode and is potentially the most responsible element in the cathode for the fade in performance and reducing cathode stability for long-term cycling.<sup>13</sup> We also perform XPS on the cycled separator of a few select electrolytes to determine if the discoloration was due to the TM deposition (Figure S4.10). In the yellow-colored area of the PF<sub>6</sub> separator we observe signals for Fe2p, Fe3p, Mn2p and Ni2p, with Fe3p having the strongest intensity (Figure S4.10b). The black edge of the PF<sub>6</sub> separator is also probed and is found to have a higher intensity of all TMs investigated. Previous reports have shown that Fe dissolution can occur when the charged Fe<sup>4+</sup> is suddenly reduced to Fe<sup>3+</sup>. The Fe ion can migrate into the tetrahedral interlayer site, with Fe<sup>3+</sup> ions easily dissolving into the electrolyte<sup>59,60</sup> and Mn dissolution occurring through disproportion reactions.<sup>61</sup> Photographs of select separators after 300 cycles at 45°C, from the cycled cells in Figure 4.1d, are also shown in Figure S4.11. The change in the separator color in the NaPF<sub>6</sub> cell is more drastic, changing the separator color from the yellow-brown color at 23°C to completely black (Figure S4.11a), consistent with the faster fade in performance at the elevated temperature (Figure 4.1d). The separators from the NaDFOB, P:D, and D:B cells at 45°C maintained a nearly pristine coloring, with a few dots of discoloration (Figure S4.11b-d). Representative TEM images are taken of the NFM 333 cathode particles in the

pristine state and after 300 cycles, at 23°C, for the PF<sub>6</sub> and D:B 75:25 cycled cells (Figure S4.12). The cathode particles retrieved from both the PF<sub>6</sub> and D:B cells have crack formations present on the particle, with an increased number of cracks on the PF<sub>6</sub> particles and extending further into the bulk of the particles. The increased severity of the cracks is consistent with the increased amount of TM reduction on the surface, subsurface, and bulk of the particles observed in the XAS analysis (Figures 4.4 and 4.5).

While NaPF<sub>6</sub> has its benefits with higher initial specific capacity and higher specific energy and power, it does not have good stability for long-term cycling. The PF<sub>6</sub> anion undergoes excessive side reactions, has a higher chance of HF formation, and produces an insufficient and unstable CEI for protecting the cathode from degradation. Meanwhile, throughout our experimentation, we observe the NaDFOB containing electrolytes to have enhanced CEI stability, greater protection against TM reduction in the surface and bulk, and suppression of TM dissolution measured on the separator and anode of the cell.

## 4.4 Conclusion

In summary, with a range of electrolyte formulations and the utilization of synchrotron spectroscopic and imaging techniques, we revealed the inefficiencies of NaPF<sub>6</sub> as a salt for stable long-term cycling and the beneficial aspects of NaDFOB as a primary, or as a secondary salt. An improved electrolyte formulation can greatly enhance the stability of the O3-NaNi<sub>1/3</sub>Fe<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cathode. With NaDFOB in the electrolyte, we observed improved long-term performance at room and elevated temperatures. At lower temperatures we observed greatly improved stability but had reduced capacity. We revealed how the improved functionality of the CEI from the oligomerization of the DFOB anion reduced the Na cell's impedance, suppressed TM cation reduction on the surface and in the bulk after long-term cycling, and maintained a highly stable

CEI that mitigated TM dissolution. Through our electrolyte formulation and engineering, we found a synergistic combination between NaDFOB and NaBF<sub>4</sub>, which leverages the beneficial qualities of both salts to improve the long-term battery performance. This study shows that deeper understanding of the cathode-electrolyte interfacial chemistry is necessary for improving the cathode/electrolyte compatibility for sodium batteries. Further investigation will be necessary to understand the electrolyte's compatibility with the Na metal anode as well as to determine the future use of NaDFOB electrolytes for practical sodium batteries.

## 4.5 Experimental Section

### 4.5.1 Materials Synthesis

The NaNi<sub>1/3</sub>Fe<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cathode materials were synthesized using a co-precipitation method followed by calcination. First, the acidic metal sulfate solutions were prepared using 0.033 M NiSO<sub>4</sub>·6H<sub>2</sub>O (Sigma Aldrich, 99.99%), 0.033 M FeSO<sub>4</sub> · 7H<sub>2</sub>O (Sigma Aldrich, 98%), and 0.033 M MnSO<sub>4</sub>·H<sub>2</sub>O (Sigma Aldrich, 99%) as the raw materials dissolved in 100 mL H<sub>2</sub>O. The starting solution (40 mL NaOH and pH value adjusted to 10.5 using sulfuric acid) and base solution (100 mL NaOH/NH<sub>3</sub> · H<sub>2</sub>O aqueous solution with a molar ratio of NaOH/NH<sub>3</sub> =2.4 (0.2 m NaOH). The transition metal solution and base solution were simultaneously pumped into the starting solution at a drop rate of 2 mL min<sup>-1</sup> with continuously stirring at 55 °C under N<sub>2</sub> protection. The drop rate of the base solution was frequently tuned to keep the pH at 10.5 ± 0.2. The precipitate was collected, washed, and filtered with DI water and dried in a vacuum oven overnight at 100 °C. The dried precursor was then thoroughly mixed with nanosized Na<sub>2</sub>CO<sub>3</sub> (the molar ratio of TM/Na was 1:1.05), transferred into a box furnace and calcined at 850 °C for 12 h. Electrolyte formulations were calculated for a total of 1 M concentration (w:w ratios) and dissolved in PC solvent. NaDFOB

was synthesized through the reaction of  $\text{Na}_2\text{C}_2\text{O}_4$  (Sigma-Aldrich) and  $\text{BF}_3 \cdot \text{ether}$  (Sigma Aldrich) in acetonitrile, which has been described in ref 39.  $\text{NaPF}_6$  and  $\text{NaBF}_4$  were obtained from Sigma Aldrich (98%).

#### 4.5.2 Material Characterization

For synchrotron XRD, XAS, and XFM experiments, electrodes from disassembled discharged coin cells were retrieved inside an Ar-filled glovebox and sealed with Kapton tapes. XRD patterns were collected in beamline 11-3 at the Stanford Synchrotron Radiation Light- source. A  $\text{LaB}_6$  sample was placed in the same location as the other sample and was used to calibrate the diffraction configuration. 2D MAR345 diffraction images were converted to 1D diffraction patterns based on the calibration parameters obtained from the  $\text{LaB}_6$  diffraction pattern. Hard XAS measurements (Ni, Mn, and Fe K-edge XANES and EXAFS) were performed on the electrodes in transmission mode at the beamline 20-BM-B of the advanced photon source (APS) at Argonne National Laboratory. The incident beam was monochromatized by using a Si (111) fixed-exit and a double-crystal monochromator. Energy calibration of each spectrum was made by aligning the first derivative maximum of a reference Ni, Mn, Fe XANES spectra collected simultaneously from the metal foils in the reference channel. Soft XAS measurements were performed on the 31-pole wiggler beamline 10–1 at Stanford synchrotron radiation lightsource (SSRL) using a ring current of 350 mA and a  $1000 \text{ L mm}^{-1}$  spherical grating monochromator with  $20 \text{ }\mu\text{m}$  entrance and exit slits, providing  $\approx 10^{11} \text{ ph s}^{-1}$  at  $0.2 \text{ eV}$  resolution in a  $1 \text{ mm}^2$  beam spot. The data were acquired under ultrahigh vacuum ( $10^{-9} \text{ Torr}$ ) in a single load at room temperature using TEY, where the sample drain current was collected, and in the FY, where a silicon diode (IRD AXUV- 100) was used to collect the FY positioned near the sample surface. All spectra were normalized by the current from freshly evaporated gold on a fine grid positioned upstream of the main chamber. XAS

samples were mounted on an aluminum sample holder with double-sided carbon tape in an Ar-filled glove box and transferred to the load-lock chamber in a double-contained container, using a glove bag purged with argon for the transfer. The X-ray fluorescence mapping was measured at the microprobe hard X-ray 2-ID-D beamline at APS. The samples are raster-scanned by a submicrometer focused X-ray beam with a photon energy of 10 keV. The fluorescent X-rays are detected by a single- element Si-drift Vortex detector. The raw data were processed and quantified by MAPS. TEM images were acquired on a JEOL 2100 TEM operated at 200 keV. XPS characterization was performed on a PHI VersaProbe III scanning XPS microscope using monochromatic Al K-alpha X-ray source (1486.6 eV). Samples were transferred from an Ar-filled glove box to the XPS ultrahigh vacuum chamber via a vacuum transfer vessel. All binding energies were referenced to C-C peak at 284.8 eV.

#### **4.5.3 Electrochemical Characterization**

The NFM electrode was prepared with 85% active material, 10% carbon black, and 5% PVDF binder. The PVDF solution was prepared with N-methyl 2-pyrrolidone (NMP) as the solvent. The cathode slurry for NFM was prepared by mixing the PVDF solution with the cathode active material and carbon black powder. The slurry was mixed in a Speedmixer for a set amount of time to ensure a homogeneous mixture. The slurry was casted onto carbon-coated Al foil using the doctor blade casting method at 70 °C. The dried casted electrode was cut to 10 mm diameter electrodes and dried in a vacuum oven overnight at 120 °C. The dried electrodes were stored in an Ar-filled glovebox. Total active material mass loading for the NFM cathodes was  $\sim 4 \text{ mg cm}^{-2}$ . 1C was defined as fully charging the cathode in 1 h corresponding to a specific current density of 120 mA g<sup>-1</sup> for the NFM cathode. CR2032 coin-cells were assembled in an Ar-filled glovebox with the 1 M electrolytes in PC solvent. The NFM cathodes were combined with the Na metal foil discs

with glass fiber separator and the volume of the electrolyte was in excess. All coin cells were assembled in an Ar-filled glovebox. LANDT and MACCOR battery testers and software were utilized to collect all Na cell cycling data. Electrochemical impedance spectroscopy measurements were performed on a Princeton Applied Research VersaSTAT 4.

## **4.6 Acknowledgements**

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## 4.7 Supporting Information

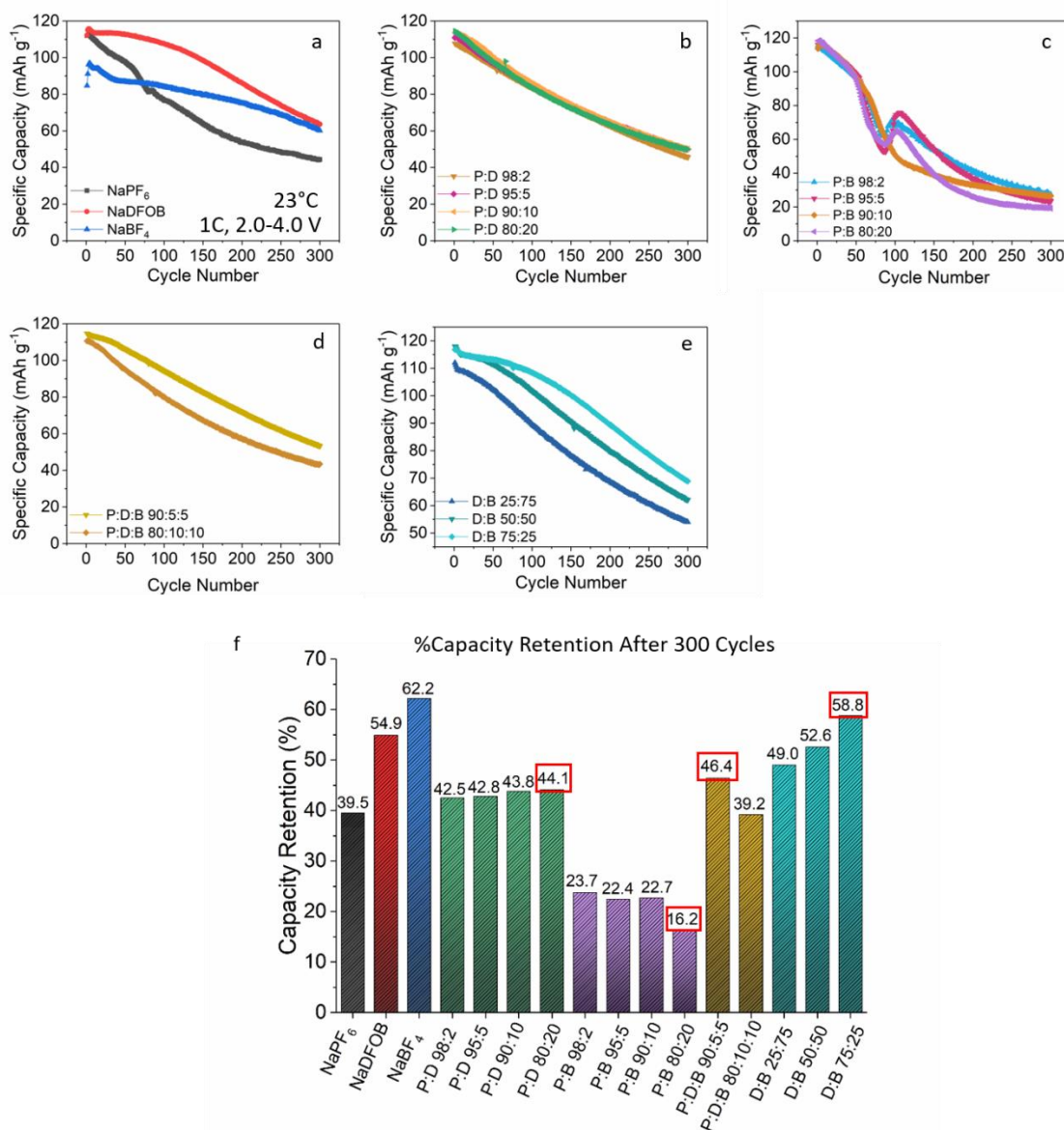


**Figure S4.1)** Electrolyte performance preliminary overview. Discharge capacity, as a function of cycle number for the a) single salt, b) P:D series, c) P:B series, d) P:D:B series, and e) D:B series electrolyte compositions and f) % capacity retention after 300 cycles with the down-selected electrolytes for further investigation highlighted in red boxes and bar graph coloring matching the colors of the down-selected compositions in the main text. These electrolytes are chosen due to having the best capacity retention from each group, with the exception of P:B 80:20. The Na cells were cycled at a 1C rate with a voltage window of 2.0 – 4.0 V at 23°C.

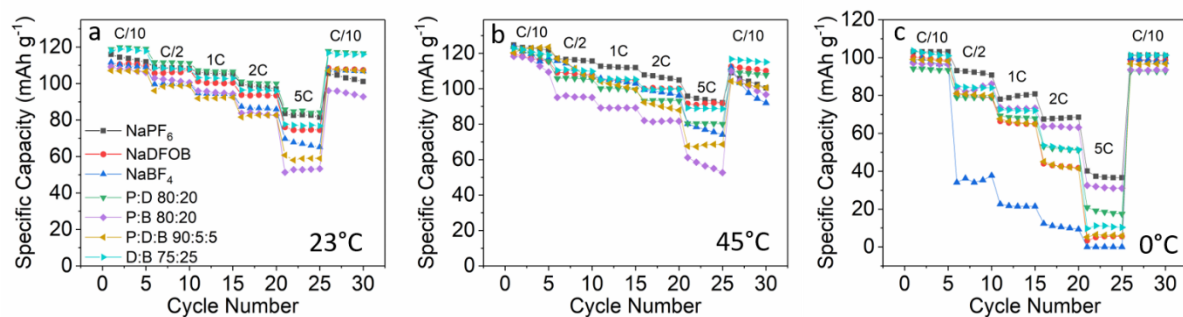


**Figure S4.2)** Rate capability of the down-selected electrolytes at current density range of C/10 to 5C and at selected temperatures a) 23°C b) 45°C and c) 0°C.

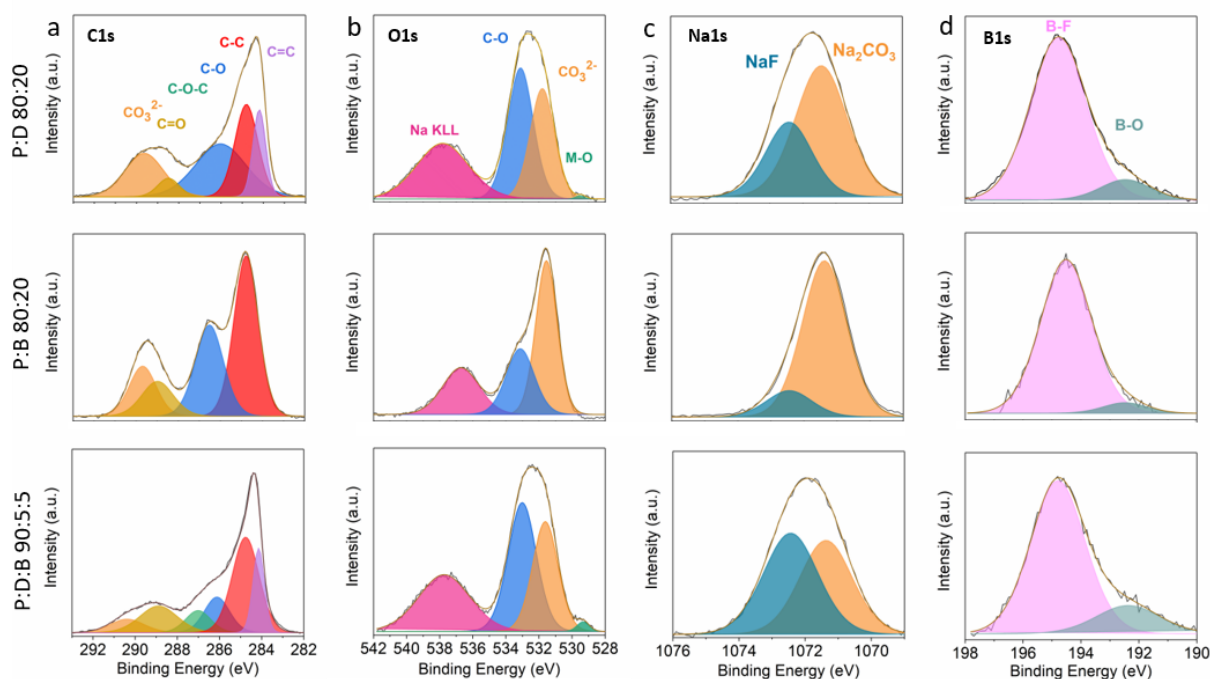


**Figure S4.3)** XPS characterization of the cycled NFM 333 cathode surface cycled with P:D 80:20, P:B 80:20, and P:D:B 90:5:5 electrolytes after 300 cycles at 23°C. a) C 1s, b) O 1s, c) B 1s, and d) B 1s XPS spectra.

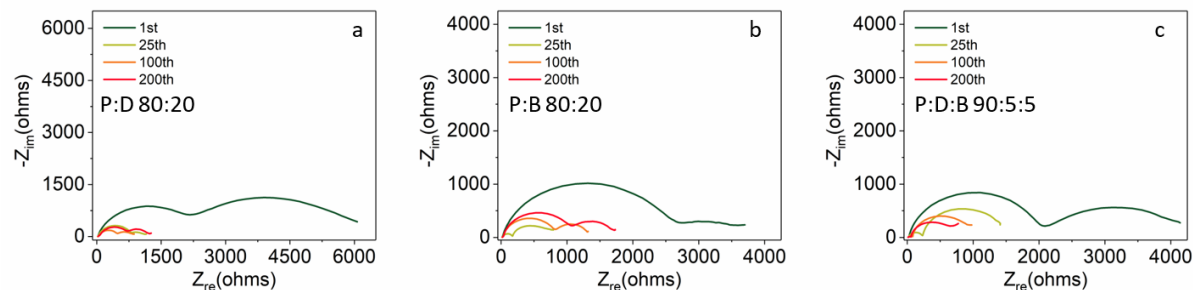


**Figure S4.4)** EIS of the NaNFM 333 Na cell after the 1<sup>st</sup>, 25<sup>th</sup>, 100<sup>th</sup>, and 200<sup>th</sup> cell cycles at 23°C for a) P:D 80:20, b) P:B 80:20, and c) P:D:B 90:5:5 electrolytes.

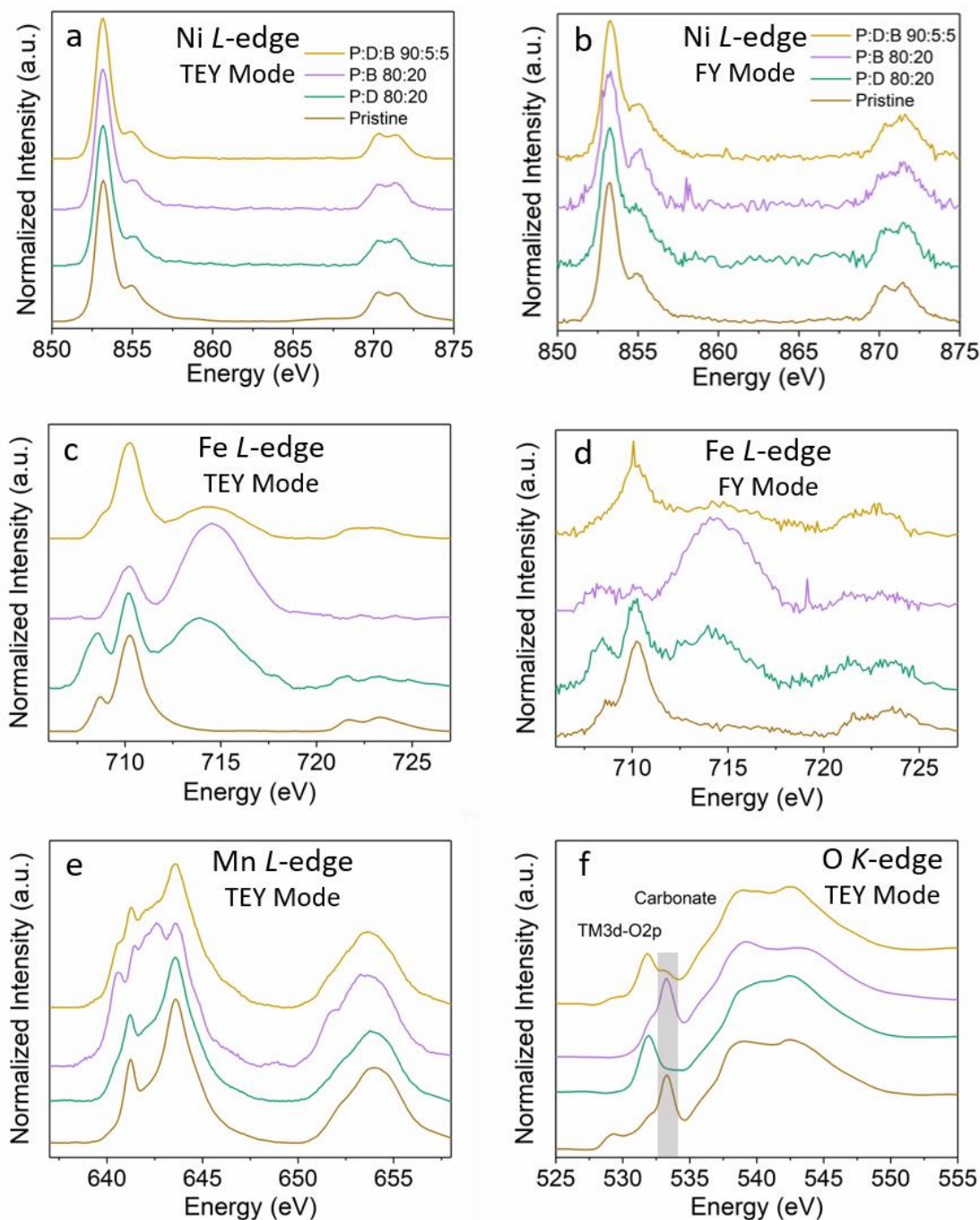


**Figure S4.5)** Interfacial chemistry analysis using soft x-ray absorption spectra of the NFM333 cathode at pristine condition and after 300 cycles at 23°C for the P:D 80:20, P:B 80:20, and P:D:B 90:5:5 electrolytes in the discharged state for Ni a) TEY and b) FY modes, Fe c) TEY and d) FY modes, and Mn e) TEY mode L-edges and f) O K-edge TEY mode with the grey bar highlighting the peaks for carbonate species.

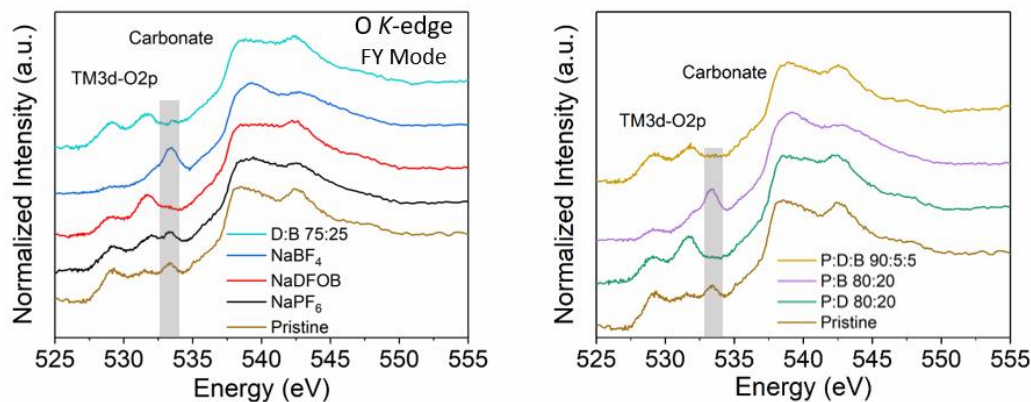


**Figure S4.6)** Interfacial chemistry analysis using soft x-ray absorption spectra of the NFM333 cathode at pristine condition and after 300 cycles at 23°C O K-edge spectra in the FY mode for all electrolyte compositions in the discharged state with the grey bar highlighting the peaks for carbonate species.

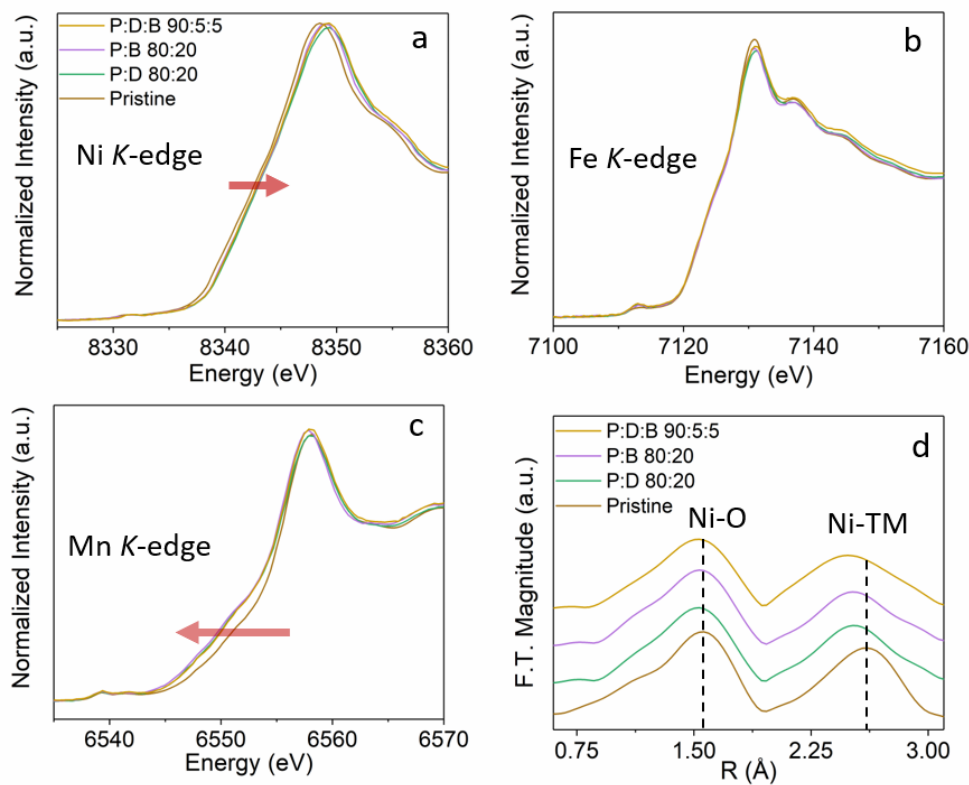


**Figure S4.7)** Oxidation-state evolution of the transition metals using x-ray absorption near edge structure (XANES) spectra the a) Ni K-edge, b) Fe K-edge, and c) Mn K-edge of the NFM333 cathode at the pristine state and after 300 cycles with P:D 80:20, P:B 80:20, and P:D:B 90:5:5 the electrolytes in the discharged state. The arrows indicate the oxidation state shift from the pristine state after cycling. Fourier-transformed extended X-ray absorption fine structure (EXAFS) of d) Ni after cycling, where the dashed lines show the peak positions for the pristine sample.

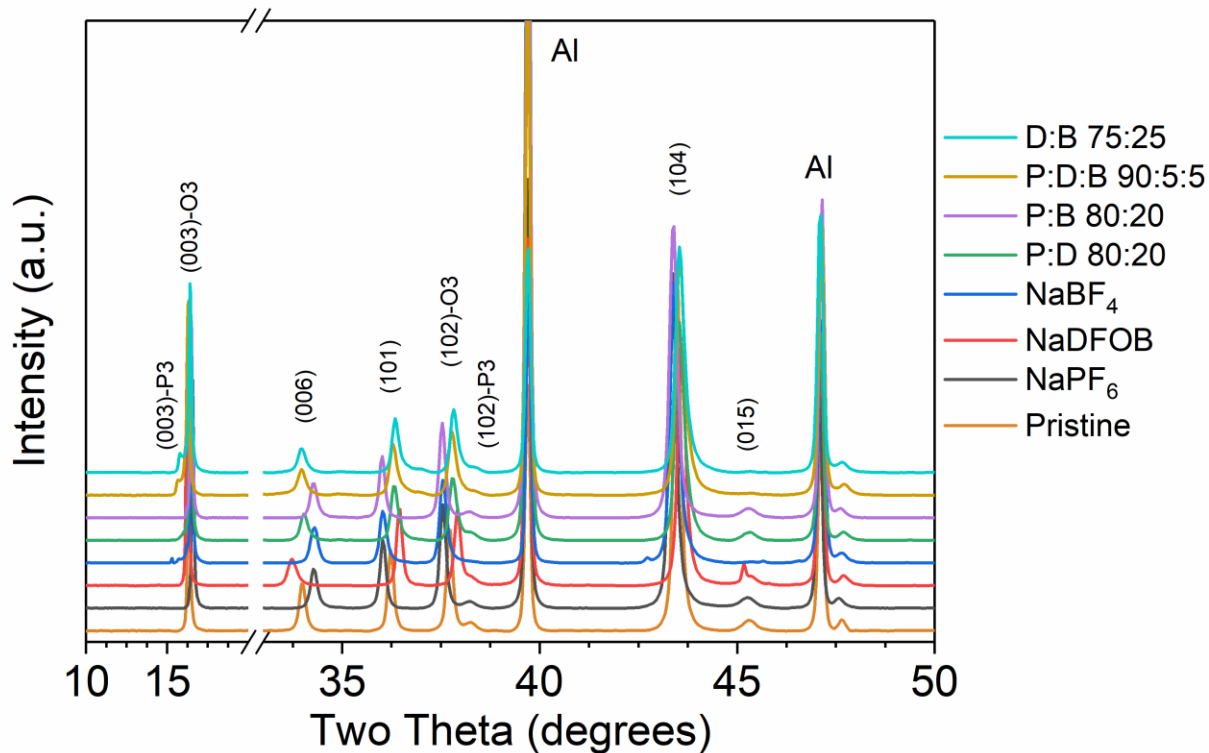


**Figure S4.8)** X-ray diffraction patterns of NFM333 cathodes cycled with the different electrolyte combinations in Na cells. The patterns were collected after 300 cycles at rate of 1C with the voltage window of 2.0–4.0 V and at 23°C.

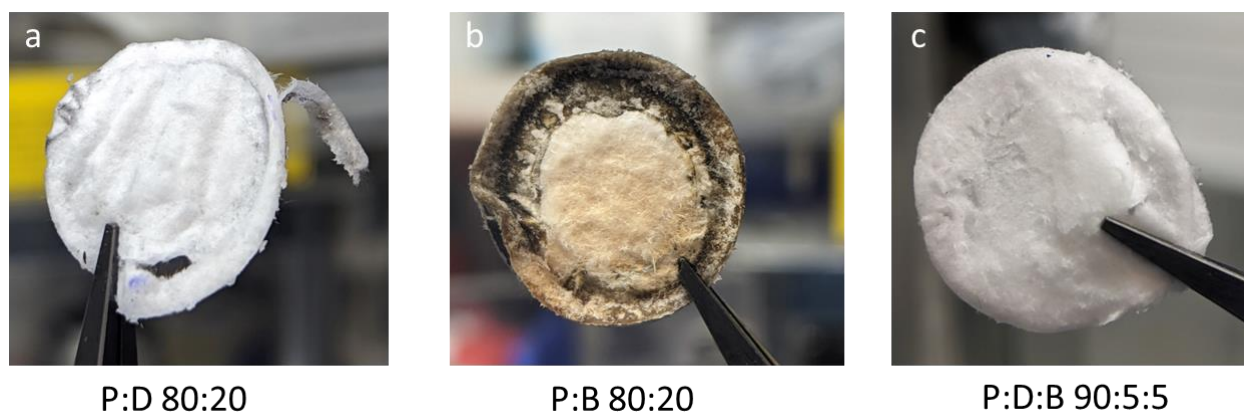


**Figure S4.9)** Photographs of the separators, facing the cathode side, after 300 cycles at 23°C highlighting the discoloration from TM dissolution for a) P:D 80:20, b) P:B 80:20, and c) P:D:B 90:5:5 electrolytes.

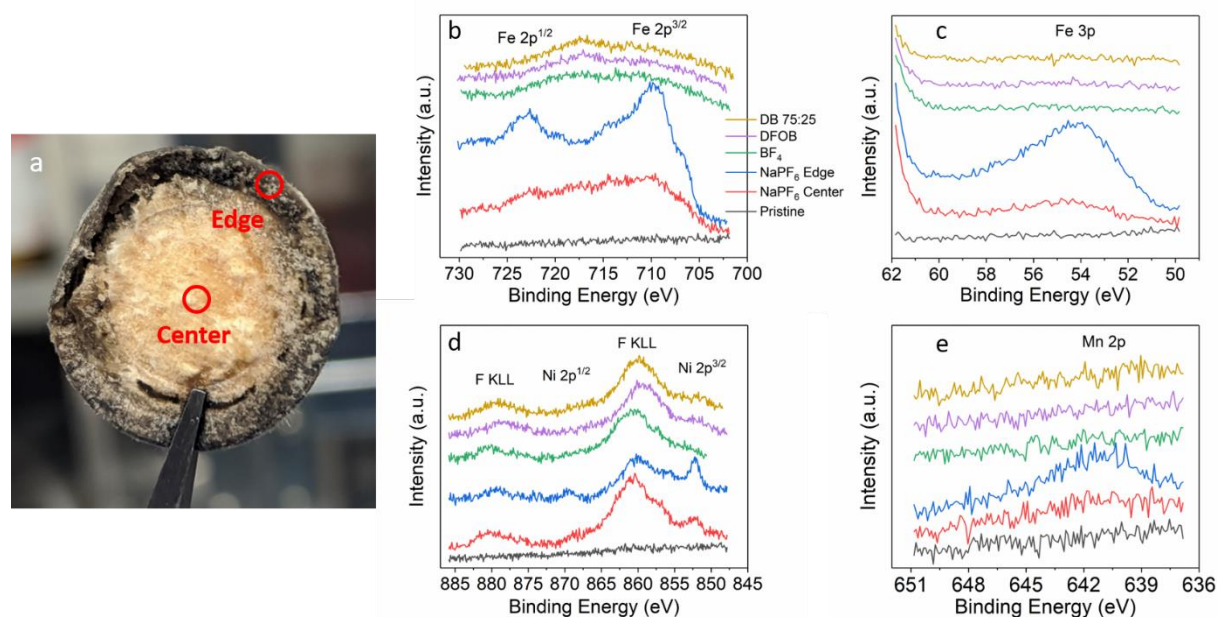


**Figure S4.10)** XPS analysis of the separators after 300 cycles at 23°C of the Na cell using the NaPF<sub>6</sub>, NaBF<sub>4</sub>, NaDFOB, and D:B 75:25 electrolytes. a) Photograph of the separator from the NaPF<sub>6</sub> Na cell showing the center and edge positions measured. a) The Fe 2p b) Fe 3p, c) Ni 2p, and d) Mn 2p spectra of separators of the different electrolytes. The remaining electrolytes were all measured in the center position of the separator.

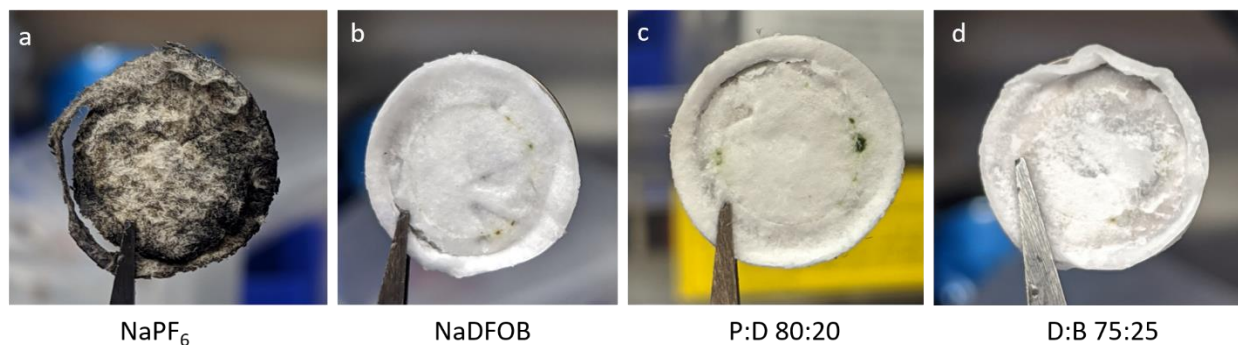


**Figure S4.11)** Photographs of the separators, facing the cathode side, after cycling at 45°C for a) NaPF<sub>6</sub>, b) NaDFOB, c) P:D 80:20, and d) D:B 75:25 electrolytes, highlighting the enhanced cathode stability and suppression of TM dissolution from the utilization of NaDFOB salt for the pure electrolyte or as a secondary salt.

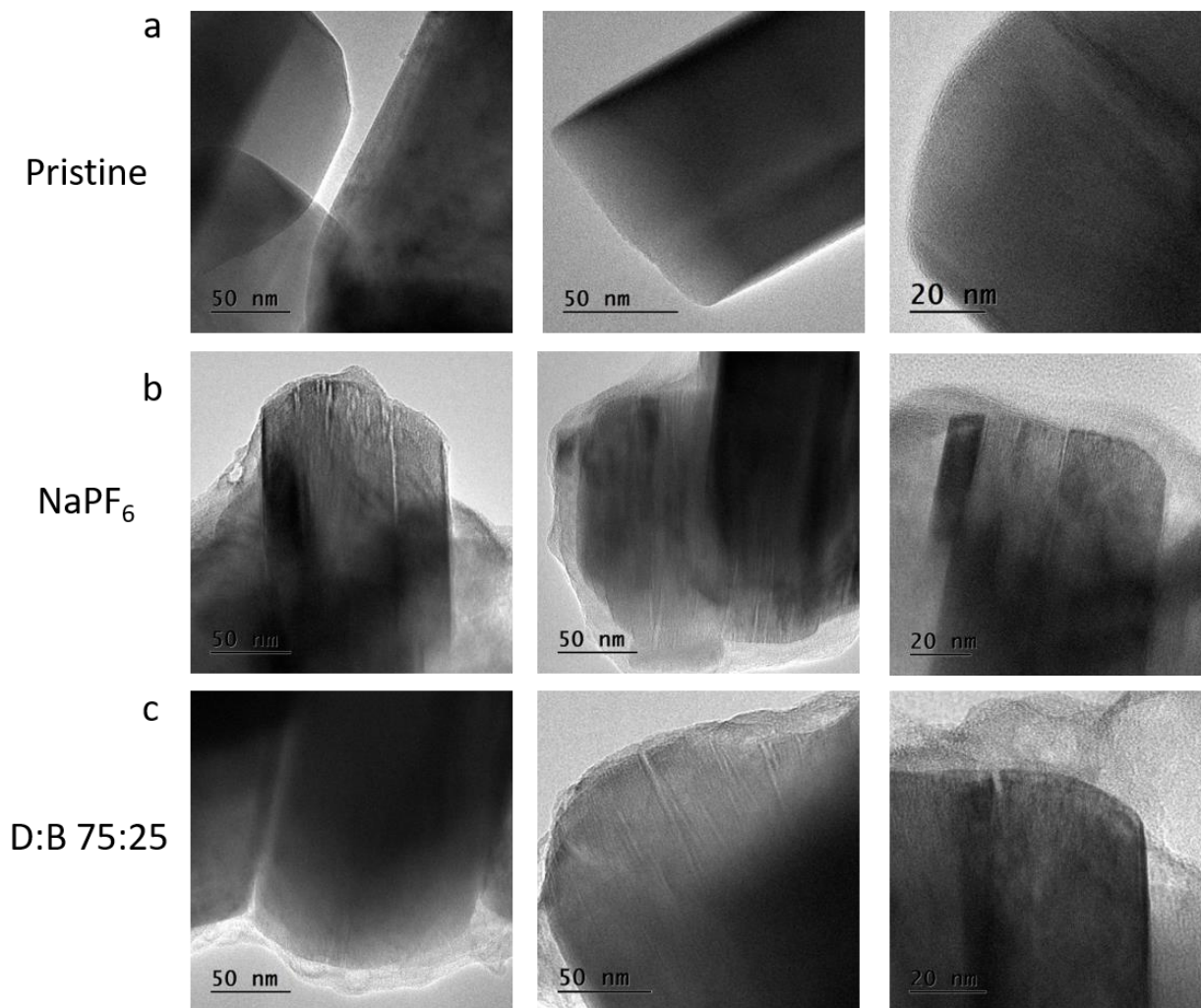


**Figure S4.12)** Representative TEM images NFM 333 cathode particles with different magnifications at the a) pristine state and after 300 cycles at 23°C using b) NaPF<sub>6</sub> and c) D:B 75:25 electrolytes observing crack formation and propagation along the surface of the cathode particles.

**Table S4.1)** Capacity retention of the NFM Na cells from the rate capability measurements in Figure S2. The capacity retention (%) was calculated between the average of the initial and final 5 cycles at a C/10 rate at 23°C, 45°C, and 0°C.

| <b>Sample \ Temperature</b> | <b>23°C</b> | <b>45°C</b> | <b>0°C</b> |
|-----------------------------|-------------|-------------|------------|
| <b>NaPF<sub>6</sub></b>     | 89.9        | 82.8        | 98.4       |
| <b>NaDFOB</b>               | 98.3        | 94.9        | 99.8       |
| <b>NaBF<sub>4</sub></b>     | 96.8        | 79.4        | 95.6       |
| <b>P:D 80:20</b>            | 98.9        | 91.1        | 98.6       |
| <b>P:B 80:20</b>            | 86.9        | 79.9        | 96.9       |
| <b>P:D:B 90:5:5</b>         | 99.9        | 86.6        | 97.2       |
| <b>D:B 75:25</b>            | 98.6        | 95.6        | 99.9       |

**Table S4.2)** Linear combination fitting of the % of the Mn oxidation state of the NaNFM 333 cathodes in the pristine state and after 300 cycles at 23°C. The Mn<sup>2+</sup>, Mn<sup>3+</sup>, and Mn<sup>4+</sup> references were from MnO, Mn<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub>, respectively.

| <b>Sample \ Oxidation State (%)</b> | <b>+2</b> | <b>+3</b> | <b>+4</b> |
|-------------------------------------|-----------|-----------|-----------|
| <b>Pristine</b>                     | 10.6      | 0         | 89.4      |
| <b>NaPF<sub>6</sub></b>             | 21.3      | 23.6      | 55.1      |
| <b>NaDFOB</b>                       | 14.3      | 0         | 85.7      |
| <b>NaBF<sub>4</sub></b>             | 18.4      | 21.5      | 60.1      |
| <b>P:D 80:20</b>                    | 24.5      | 0         | 75.5      |
| <b>PB 80:20</b>                     | 31.9      | 37.1      | 31.0      |
| <b>P:D:B 90:5:5</b>                 | 14.1      | 28.6      | 57.3      |
| <b>D:B 75:25</b>                    | 14.5      | 0         | 85.5      |

**Table S4.3)** Mean concentration ( $\mu\text{g cm}^{-2}$ ) calculated from XFM analysis of transition metals measured sodium metal anode after 300 cycles at 23°C.

| Sample                  | Mean Concentration ( $\mu\text{g cm}^{-2}$ ) |        |        |
|-------------------------|----------------------------------------------|--------|--------|
|                         | Ni                                           | Fe     | Mn     |
| <b>NaPF<sub>6</sub></b> | 7.384                                        | 80.131 | 1.586  |
| <b>NaDFOB</b>           | 0.098                                        | 0.323  | 0.115  |
| <b>NaBF<sub>4</sub></b> | 0.196                                        | 0.934  | 0.188  |
| <b>P:B 80:20</b>        | 1.853                                        | 15.477 | 0.375  |
| <b>P:D 80:20</b>        | 0.146                                        | 0.464  | 0.639  |
| <b>P:D:B 90:5:5</b>     | 0.075                                        | 0.181  | 0.106  |
| <b>D:B 75:25</b>        | 0.053                                        | 0.129  | 0.0757 |

**Table S4.4)** Mean concentration ( $\mu\text{g cm}^{-2}$ ) of transition metals measured from ICP-MS analysis of the separator after 300 cycles at 23°C.

| Sample                  | Mean Concentration ( $\mu\text{g cm}^{-2}$ ) |         |        |
|-------------------------|----------------------------------------------|---------|--------|
|                         | Ni                                           | Fe      | Mn     |
| <b>NaPF<sub>6</sub></b> | 83.938                                       | 545.397 | 24.575 |
| <b>NaDFOB</b>           | 11.600                                       | 15.063  | 4.135  |
| <b>NaBF<sub>4</sub></b> | 8.796                                        | 10.919  | 3.678  |
| <b>P:B 80:20</b>        | 93.677                                       | 1209.46 | 20.783 |
| <b>P:D 80:20</b>        | 11.991                                       | 7.610   | 5.295  |
| <b>P:D:B 90:5:5</b>     | 13.922                                       | 10.503  | 7.012  |
| <b>D:B 75:25</b>        | 10.454                                       | 6.584   | 3.437  |

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## 5. Probing the Electrochemical Properties and Sodium Metal Anode-Electrolyte Interfacial Chemistry of Sodium Borate Salts

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### 5.1 Abstract

Stabilizing the Na metal anode is a challenge necessary for the development of next-generation Na metal batteries. This work highlights selected sodium borate salt electrolytes, such as sodium tetrafluoroborate ( $\text{NaBF}_4$ ) and sodium difluoro(oxolato)borate ( $\text{NaDFOB}$ ), which have shown promising results in stabilizing Na cathodes materials and the Na metal anode for long-term cycling. In this work, we investigate the electrochemical properties of our selected electrolyte formulations to determine the characteristics that can enable a high-rate performance, long cycle life, and effectively passivate Na metal anode. Through electrochemical diagnostics and X-ray photoelectron spectroscopy, we demonstrate that the  $\text{NaDFOB}$  salt enables favorable anode-electrolyte interactions and passivation of the Na metal anode at various temperatures and current densities. Even in “lean” Na anode conditions, the  $\text{NaDFOB}$  electrolytes deliver the best electrochemical performance and cycle life. The DFOB anion helps facilitate the formation of a robust solid-electrolyte interphase (SEI) that provides structural and chemical stability to the Na metal and helps enable long-term cycling capabilities.

## 5.2 Introduction

The ever-increasing demand for large scale grid energy storage has brought attention to sodium batteries as a promising alternative in recent years due to their competitive economic and environmental aspects.<sup>1-4</sup> Although lithium metal is one of the most promising materials to achieve high energy density batteries, Li resources are less abundant and not evenly distributed in the Earth's crust and can affect access and applications for large-scale applications.<sup>5,6</sup> Na metal, on the other hand, is more widely abundant and distributed in the Earth's crust and is more cost effective for large-scale applications. The high theoretical capacity (1,166 mAh g<sup>-1</sup>) and low electrochemical potential (-2.71 vs. SHE) helps enable Na metal as a promising candidate for the design of high energy density batteries.<sup>7,8</sup> However, the electrochemical performance and safety issues of Na metal have been concerns for commercial applications for Na batteries. One of the key research efforts to stabilize Na metal for practical applications is the modification of the electrolyte through the design of multi-salt electrolytes or the use of small amounts of sacrificial electrolyte additives to create a chemically and mechanically stable SEI on the anode surface.<sup>7,9-</sup>

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Li and Na hexafluorophosphate (PF<sub>6</sub>) is one of the most common salts in the literature due to its high solubility, wide electrochemical stability window (ESW), and relatively high ionic conductivity.<sup>12,17</sup> However, the production of HF as the byproduct of the decomposition of the PF<sub>6</sub> anion when reacting with trace amounts of water is well established.<sup>18-20</sup> Throughout the past few decades Li and Na borate salts have shown promising results for the formation of a stable electrode-electrolyte interphase and prolong cycling stability in both Li and Na cathodes materials and metal anodes.<sup>21-26</sup> The high ionic dissociation energy of the borate salts increases the chemical stability of the salt in the electrolyte and is less reactive against Li and Na metal.<sup>27</sup> In particular,

sodium tetrafluoroborate ( $\text{NaBF}_4$ ) and sodium difluoro(oxolato)borate ( $\text{NaDFOB}$ ) have been reported in the literature to have good electrochemical stability, the formation of a stable passivation layer on the cathode and anode, and enhanced thermal stability at elevated temperatures.<sup>22,28,29</sup> Previous reports have shown that the DFOB anion undergoes an oligomerization pathway through a ring-opening decomposition mechanism.<sup>23,28,30</sup> The oligomer byproducts can imbed into the passivation layer and form an ionically conductive and electronically insulative electrode-electrolyte interphase to promote Li- or Na ion transport and suppress undesired reactions with the electrolyte through electron transfer.<sup>23,28,30</sup> Previously, we have investigated the design of electrolyte engineering and interfacial chemistry for cathode-electrolyte interactions and have shown that including  $\text{NaDFOB}$  in the electrolyte compositions as the primary or auxiliary salt has improved cathode stabilization (Chapter 4).

Herein, we continue the investigation of our selected electrolyte formulations of  $\text{NaPF}_6$ ,  $\text{NaBF}_4$ , and  $\text{NaDFOB}$  salts and focus on the electrochemical properties of the electrolyte and the anode-electrolyte interfacial interactions against Na metal. We find that the inclusion of  $\text{NaDFOB}$  as a primary or auxiliary salt generally increases the electrochemical stability and  $\text{Na}||\text{Na}$  symmetric cycling performance of the electrolyte at room and elevated temperatures. The decomposition of the DFOB anion forms a more effective passivation layer and protects the Na metal from undesired side reactions with the electrolyte. In the electrodeposition of “lean” Na-CNF composite anodes, the  $\text{NaDFOB}$  containing electrolytes had a pristine metallic color on the composite anode and enabled improved cycle life. This study demonstrates the importance of the composition of electrolyte formulations in stabilizing the anode-electrolyte interfacial chemistry and enabling long-term cyclability for sodium batteries.

## 5.3 Results and Discussion

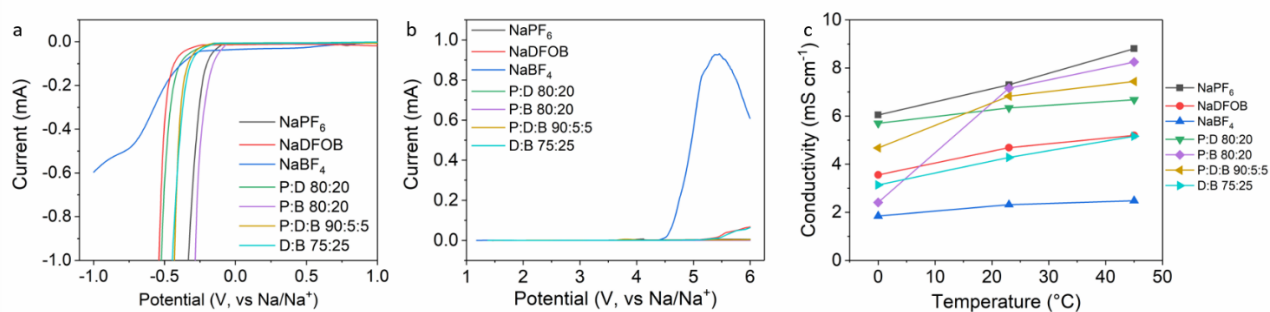


**Figure 5.1)** Electrochemical properties of electrolyte formulations. Measuring the electrochemical stability window with linear sweep voltammetry scanning the a) negative potential and b) positive potential ranges. c) Conductivity measurements of electrolytes at 0°C, 23°C, and 45°C.

### 5.3.1 Electrochemical characterization of electrolyte mixtures

The electrolyte compositions that were selected for further investigation in Chapter 4 were chosen to continue in the study of the electrochemical properties and performance and their compatibility against the Na metal anode. We formulate a variety of electrolyte compositions utilizing NaPF<sub>6</sub> (P), NaBF<sub>4</sub> (B), and NaDFOB (D) as the main sodium salts used throughout this study at 1 M total concentration dissolved in propylene (PC) carbonate. We focus on seven electrolyte compositions throughout this investigation and are named from the combination of the abbreviations of the containing salt (P, B, or D) and the ratio (w:w) to obtain 1 M concentration (e.g., P:B 80:20). In this first section, we aim to investigate the electrochemical properties and determine the effect of the auxiliary salt(s) on the electrolyte composition.

We perform linear sweep voltammetry (LSV) to measure the electrochemical stability window (ESW) of the selected electrolyte formulations at a scan rate of 1 mV s<sup>-1</sup> (Figure 5.1a,b). A wide ESW is necessary to enable the application of high-voltage cathode materials and Na metal anode for the development of high energy density batteries. The lower voltage window

(reduction potential) of the selected electrolytes ranges from approximately -0.08 V to -0.35 V vs. Na/Na<sup>+</sup> (Figure 5.1a). The electrochemical reduction potential is correlated with the lowest unoccupied molecular orbital (LUMO) energy of the salt or solvent in the electrolyte, and the compound with the lowest LUMO energy would get reduced first. The electrolytes that contained NaBF<sub>4</sub> are observed to have a lower reduction potential stability compared to their primary salt electrolytes. The NaBF<sub>4</sub> electrolyte started to get a reductive current response starting from ~0.5 V and has a larger reduction curve at approximately -0.24 V. The earlier onset reduction potential of the NaBF<sub>4</sub> salt can potentially decrease the stability of other electrolyte compositions through the formation of a pathway for electron transfer from the decomposed NaBF<sub>4</sub> salt to the other salts or solvent molecules in the electrolyte.<sup>31</sup> The addition of NaDFOB was shown to improve the containing electrolyte's reductive stability and increase the lower limit of the electrolyte's reductive potential window. The pure NaBF<sub>4</sub> electrolyte also has the lowest oxidative stability with its upper limit stability at approximately 4.52 V (Figure 5.2). The BF<sub>4</sub> anion has previously been reported to have a larger highest occupied molecular orbital (HOMO) energy, compared to the PF<sub>6</sub> anion resulting in a lower thermodynamic stability against oxidation.<sup>31</sup> The oxidation curve of pure NaDFOB and D:B 75:25 electrolytes are identical and have an improved oxidative stability, compared to NaBF<sub>4</sub>, with a positive current increasing beginning at approximately 5.45 V. The pure NaPF<sub>6</sub> electrolyte has the highest oxidation potential of our electrolyte compositions and is the most thermodynamically stable against electrolyte oxidation. Unlike in the negative sweep, the inclusion of NaBF<sub>4</sub> or NaDFOB to the NaPF<sub>6</sub> electrolytes did not have a measurable effect on the oxidative stability of the NaPF<sub>6</sub> containing electrolytes.

We next measure the ionic conductivity of the electrolytes at 0°C, 23°C, and 45°C (Figure 5.1c). A high ionic conductivity, at a range of temperatures, is necessary to achieve high power of

the battery electrodes. The salt anion can largely influence the electrolyte conductivity due to the variations in the  $\text{Na}^+$  solvation and ionic association interactions. Sodium borate anions typically have stronger ionic association due to their shorter bond length, reducing the rate of ionic dissociation and ionic mobility and increasing electrolyte viscosity.<sup>21,32</sup> The pure  $\text{NaPF}_6$  electrolyte has the highest ionic conductivity at all temperatures. The ionic conductivity of the  $\text{NaPF}_6$  electrolytes is reduced when  $\text{NaBF}_4$  and/or  $\text{NaDFOB}$  are added. At 0 °C, the conductivity of the P:B 80:20 electrolyte decreases significantly, while the decrease in conductivity of the P:D 80:20 and P:D:B 90:5:5 electrolytes are less prominent. This result suggests that the  $\text{NaBF}_4$  added to the electrolyte can have a significant effect on the electrolyte characteristics, even at small concentrations. At low temperatures,  $\text{NaBF}_4$  could potentially crash from the solution and recrystallize in the electrolyte, causing a growth in the internal impedance and reduce Na ion mobility in the mixed electrolytes. When measured at 45°C, the ionic conductivity increased for all electrolytes. The measured increase in conductivity for the  $\text{NaBF}_4$  containing electrolytes is not as significant. The additional thermal energy inputted into the electrolyte may not have been enough to increase ionic dissociation of the  $\text{NaBF}_4$  salt and would require an even higher increase in temperature, which is unsafe for practical applications of Na ion batteries.

In summary, the electrochemical properties of pure  $\text{NaBF}_4$  are found to be the worst of all electrolytes measured. It has the lowest conductivity and smallest ESW. The high reactivity of the  $\text{NaBF}_4$  in the mixed electrolytes will reduce the electrolyte's stability against the Na metal anode and decrease the electrolyte's overall electrochemical performance. On the other hand, the electrochemical characteristics of the  $\text{NaDFOB}$  electrolyte are promising. The inclusion of  $\text{NaDFOB}$  improves the electrolyte's stability against electrochemical reduction and the high oxidation voltage ~5.5 V can allow for high voltage cathode applications for high-energy density

battery applications. We next test the electrochemical performance of the electrolytes in symmetric cell analysis.

### 5.3.2 Na||Na symmetric cell electrochemical performance

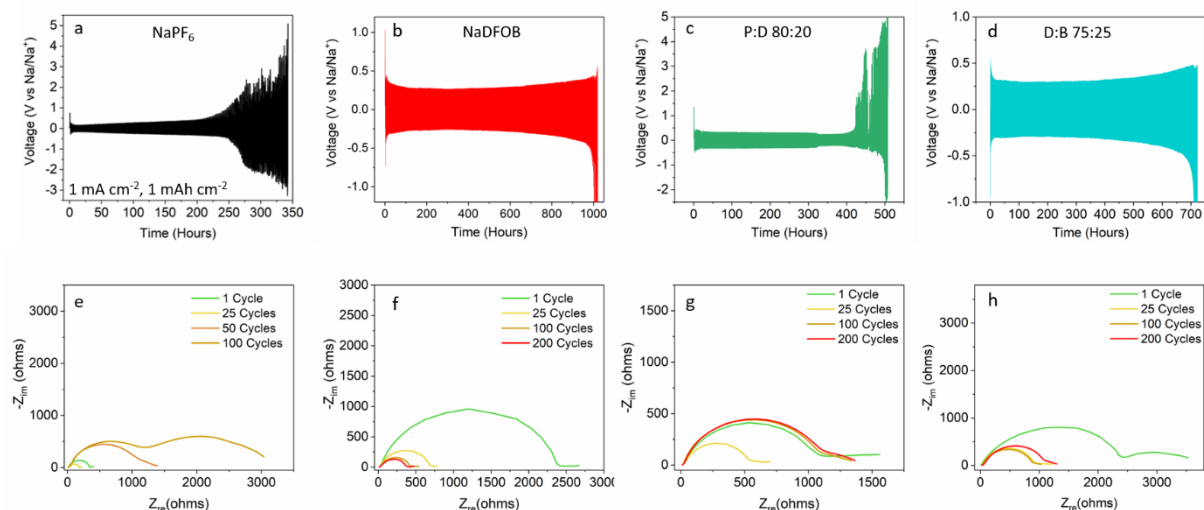


**Figure 5.2)** Galvanostatic cycling results from symmetric Na-Na cells cycled at a current density of  $1\text{ mA cm}^{-2}$  with an areal capacity of  $1\text{ mAh cm}^{-2}$  for a)  $\text{NaPF}_6$ , b)  $\text{NaDFOB}$ , c) P:D 80:20, and d) D:B 75:25 electrolytes. Electrochemical impedance spectroscopy for symmetric Na-Na cells measured during cycling for e)  $\text{NaPF}_6$ , f)  $\text{NaDFOB}$ , g) P:D 80:20, and h) D:B 75:25 electrolytes.

Sodium metal foil Na||Na symmetric cells are designed for the performance measurements throughout most of this study. The use of symmetric cells allows the observation of the anode-electrolyte interfacial reactions and the electrolyte's cycling performance and stability. Good interfacial compatibility is crucial for achieving long cycle life and reducing impedance growth in the cell. We cycle the symmetric cells at  $23^\circ\text{C}$  for a total areal capacity of  $1\text{ mAh cm}^{-2}$  at a current density of  $1\text{ mA cm}^{-2}$  and use electrochemical impedance spectroscopy (EIS) to evaluate the cell's impedance while cycling over time (Figure 5.2 and S5.1). After 125 cycles (250 hours) the pure  $\text{NaPF}_6$  cell's voltage profile begins to increase followed by the cell shorting after 350 hours, potentially from dendrite growth (Figure 5.2a). The rapid growth in the cell's overpotential is

related to an unstable and highly reactive Na-electrolyte interface.<sup>33</sup> The NaDFOB containing electrolytes have a smoother voltage profile and extended cycle life before undergoing a rapid increase in cell potential and shorting (Figure 5.2 c-d) while a decrease in cell stability and cycle life is observed in the NaBF<sub>4</sub> containing electrolytes (Figure 5.2d and Figure S5.1). As seen in the ESW measurements, the NaDFOB electrolytes have improved reductive stability at lower voltages and have better interfacial compatibility with the sodium metal anode, improving the overall cycling capabilities of the Na cells.

We then measure the EIS of the symmetric cells to observe the stability of the anode-electrolyte interface during cycling at 23°C (Figure 5.2e-h and Figure S5.1d-f). We observe two semi-circles in the EIS spectra. The left semi-circle is associated with the electrode-electrolyte interfacial resistance and the right semi-circle is related to the charge-transfer resistance.<sup>34</sup> Over increasing cycle number, the impedance measured for the NaDFOB containing electrolytes decreases as the SEI reorganizes and “optimizes” its structure on the anode’s surface, while after 25 cycles, the impedance for pure NaPF<sub>6</sub> and NaBF<sub>4</sub> electrolytes increases (Figure 5.2a and Figure S5.1d). Poor anode-electrolyte interfacial compatibility leads to an unstable SEI that is unable to effectively passivate the anode surface from undesired side reactions and promotes continuous electrolyte decomposition and impedance growth. A positive feedback loop would be established increasing rate of side reactions and decreasing cell performance. The NaBF<sub>4</sub>’s reductive instability decreases the effective cycle life of the NaBF<sub>4</sub> containing electrolyte, while the inclusion of NaDFOB produces a more robust SEI that more effectively passivates the sodium metal anode.

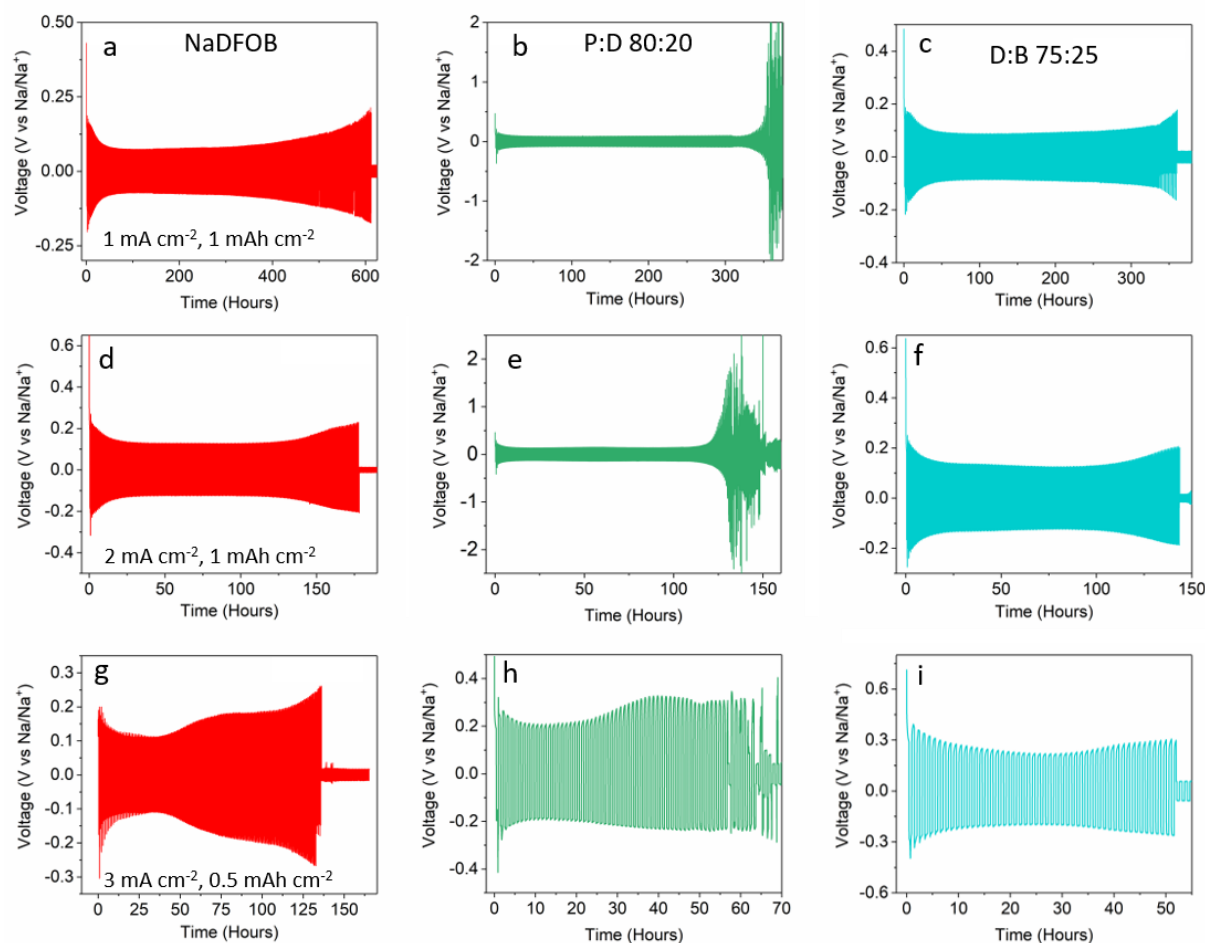


**Figure 5.3)** Elevated temperature galvanostatic cycling results from symmetric Na-Na cells at 45°C for NaDFOB, P:D 80:20, and D:B 75:25 electrolytes at a current density and areal capacity of (a-c) 1 mA cm<sup>-2</sup> and 1 mAh cm<sup>-1</sup>, (d-f) 2 mA cm<sup>-2</sup> and 1 mAh cm<sup>-1</sup>, (g-i) 3 mA cm<sup>-2</sup> and 0.5 mAh cm<sup>-1</sup>.

We then increasing temperature to 45°C to test the stability and cycling capabilities of the electrolytes under more thermally demanding conditions (Figure 5.3). Li and Na borate electrolytes have been reported to have higher thermal stability and improve electrochemical performance at elevated temperatures.<sup>28,32,35</sup> We cycle the symmetric cells at a total areal capacity of 1 mAh cm<sup>-2</sup> and at a current density of 1 mA cm<sup>-2</sup>. The cycle life for all electrolytes is reduced compared to performance at 23°C. The NaDFOB, P:D 80:20, and D:B 75:25 cells maintain good stability and are able to cycle over 300 hours before shorting with the pure NaDFOB cell having

the best stability, shorting after 600 hours (Figure 5.3a-c). On the other hand, the cycling stability of the NaPF<sub>6</sub>, NaBF<sub>4</sub>, and P:B 80:20 cells is significantly reduced and all short within the first 20-30 hours (Figure S5.2). The reduced reductive stability of both the NaPF<sub>6</sub> and NaBF<sub>4</sub> electrolytes is compounded with their poor thermal stability, increasing the rate of electrolyte reduction, side reactions with the Na metal, and potential dendritic growth. The NaDFOB salt is more thermally stable and forms a more effective passivation layer to protect the anode. At a higher current density of 2 mA cm<sup>-2</sup> and 3 mA cm<sup>-2</sup> the pure NaDFOB cells maintain the best cycling stability followed by D:B 75:25 and P:D 80:20 (Figure 5.3d-i). The higher the concentration of NaDFOB added to the electrolytes the better the cycling lifetime and stability of the symmetric cells is observed.

### 5.3.3 Probing of the Solid Electrolyte Interphase

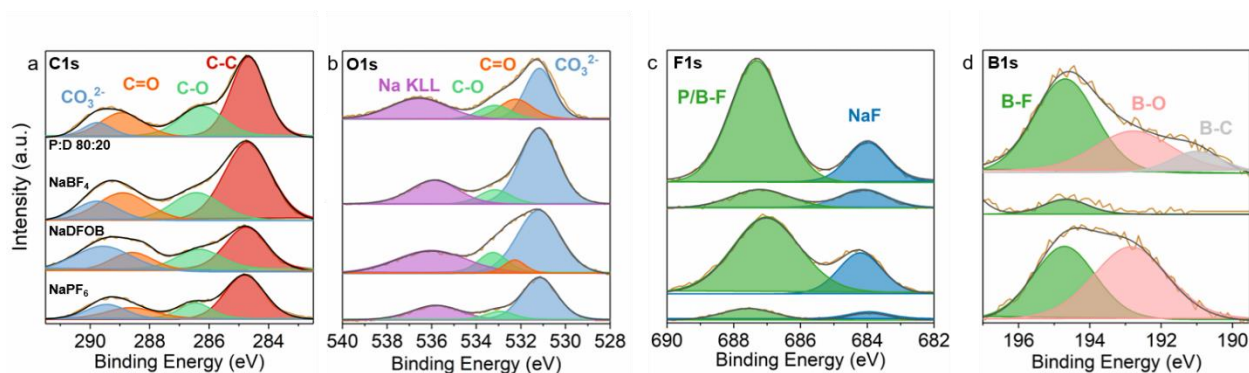


**Figure 5.4)** Probing the SEI composition on the cycled Na metal anode after 100 cycles of Na-Na symmetric cells at 23°C for the a) C 1s, b) O 1s, c) F 1s NaPF<sub>6</sub>, NaDFOB, NaBF<sub>4</sub>, and P:D 80:20, and d) B 1s spectra from the NaDFOB, NaBF<sub>4</sub>, and P:D 80:20 electrolytes (bottom to top).

The SEI on the anode is one of the main factors that can govern the overall stability and lifespan of the cell. We use X-ray photoelectron spectroscopy (XPS) analysis to explore the SEI composition of the symmetric cells after 100 cycles at 23°C for the NaPF<sub>6</sub>, NaDFOB, NaBF<sub>4</sub>, and P:D 80:20 electrolytes (Figure 5.4). The C 1s and O 1s spectra of the electrolytes do not show a large variation in the chemical species present in the SEI, which is primarily from the

decomposition of the carbonate solvent (Figure 5.4a,b).<sup>36</sup> In the F 1s spectra, we observe a large difference in the signal intensity of the two peaks observed assigned to the P/B-F and NaF (Figure 5.4c). Higher quantities of NaF have been attributed to better mechanical stability to prevent sodium deformation and improve sodium plating and as an electronic insulator to prevent the electrolyte from being reduced.<sup>23,37,38</sup> The increased intensity for the P-F/B-F peak on the anodes cycled in the NaDFOB and P:D 80:20 electrolytes can be attributed to the decomposition product of the DFOB anion, which can oligomerize with other SEI components and form a more robust passivation layer to protect the anode from further reactions and suppress dendrite formation.<sup>26,39</sup> The strong intensities for the B-F and B-O peaks present in the SEI of the anode's cycled in the NaDFOB and P:D 80:20 electrolytes would be from the presence of the boron-bearing oligomers, as well as sodium borate species that add structural stability to the SEI.<sup>21,28,40</sup> The weak intensity of the B-F peak in the NaBF<sub>4</sub> anode suggest that the salt is unable to form an SEI layer that can effectively passivate the anode.

#### **5.3.4 Electrolyte effect on electrodepositing “lean” Na-CNF composite anodes**

The composition of the electrolyte has a significant effect on the plating/stripping characteristics of the alkali metal anode such as morphology and reactivity while cycling.<sup>14,41,42</sup> The electrochemical properties of the electrolytes can affect the Na nucleation energy to begin Na metal seeding and growth during electrodeposition.<sup>43,44</sup> The electrolytes with higher energy barriers for ion dissociation or lower conductivity have a larger resistance and require a higher nucleation overpotential for Na metal electrodeposition. The SEI formed during electrodeposition must have high mechanical stability to handle the volumetric expansion of the electroplated Na metal and to minimize electrochemical oxidizing reactions with the Na metal.<sup>43–46</sup> In our previous study, shown in Chapter 3, we investigate “lean” (3 mAh cm<sup>-2</sup>) Li and Na composite anodes using

a  $\text{PF}_6$  based electrolyte. Our previous findings are that the electrodeposited sodium metal, in an  $\text{NaPF}_6$  electrolyte, is unstable due to reacting with the electrolyte during electrodeposition. We continue our study by designing the “lean” sodium composite anodes with our selected electrolytes compositions and investigate the physical characteristics and electrochemical performance of the composite anodes.

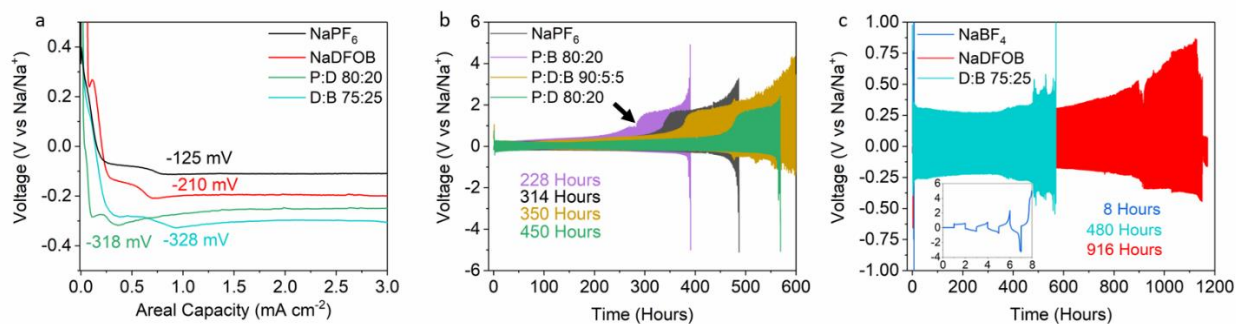


**Figure 5.5)** Probing the electrolyte stability of electrodeposited “lean” Na//Na-CNF composite anode cycling performance with total deposited areal capacity of  $3 \text{ mAh cm}^{-2}$  and current density of  $0.5 \text{ mA cm}^{-2}$ . a) Electrodeposition profile for  $\text{NaPF}_6$ ,  $\text{NaDFOB}$ , P:D 80:20, and D:B 75:25 electrolytes with measured nucleation overpotential labeled. Na//Na-CNF cycling performance for b) pure  $\text{NaPF}_6$  and  $\text{NaPF}_6$  mixed composition electrolytes and c)  $\text{NaBF}_4$ ,  $\text{NaDFOB}$ , and D:B 75:25 electrolytes with the times of the beginning of rapid cell overpotential growth listed and the arrow highlighting an example of the sudden jump in overpotential.

We electrodeposit a total areal capacity of  $3 \text{ mAh cm}^{-2}$  of Na metal onto the carbon nanofiber (CNF) substrate at a current density of  $0.25 \text{ mA cm}^{-2}$ . The nucleation overpotential for the  $\text{NaPF}_6$  electrolyte is the lowest of all electrolyte compositions at -125 mV (Figure 5.5a). The  $\text{NaPF}_6$  electrolyte has the lowest ionic dissociation energy barrier and the highest conductivity and would have the least resistance for the nucleation of Na metal. The nucleation overpotentials for the  $\text{NaDFOB}$ , P:D 80:20, and D:B 75:25 electrolytes are -210 mV, -318 mV, and -328 mV, respectively (Figure 5.5a). The relative bulkiness of the DFOB anion and higher dissociation energy barrier would increase the overpotential to begin nucleation. The mixed electrolytes require a higher overpotential to begin the Na nucleation phase, similar to the higher overpotential

observed in the symmetric cycling stripping/plating profiles (Figure 5.2 and Figure S5.1). However, the increase in the overpotential is not as severe when  $\text{NaBF}_4$  is added to  $\text{NaPF}_6$  (Figure S5.3). The P:B 80:20 and P:D:B 90:5:5 electrolytes have an overpotential of -152 mV and -245 mV, which is much lower compared to the P:D and D:B electrolytes. When dissociated,  $\text{NaBF}_4$  has a higher ionic mobility than  $\text{NaDFOB}$ , due to its smaller size, and can potentially help lower the nucleation overpotential. However, the pure  $\text{NaBF}_4$  electrolyte, having the lowest electrochemical reduction potential, lowest conductivity, and highest ionic dissociation energy is found to not to be capable for practical electrodeposition for the composite anode and shorts the cell (Figure S5.3).

Photographs of the composite anodes and of select glass fiber separators were taken after electrodeposition (Figure S5.4). The composite anode with the pure  $\text{NaDFOB}$  electrolyte has the most pristine and metallic color, while the pure  $\text{NaBF}_4$  electrode is the most heavily oxidized and has a dark grey color (Figure S5.4). The separator from the  $\text{NaBF}_4$  cell had “dead” oxidized sodium plated on both the CNF facing side and the Na metal facing side. The P:B, P:D:B, and D:B electrodes are darker and more oxidized, compared to the pure  $\text{NaPF}_6$  and  $\text{NaDFOB}$  electrolytes. The inclusion of  $\text{NaBF}_4$  reduces the reductive stability and increases the reaction against the Na metal during electrodeposition and can reduce the effectiveness of the electrodeposited Na metal. The P:B 80:20 separator is the only other separator that has specks of “dead” sodium metal implanted into the separator (Figure S5.4).

After electrodeposition, we retrieve the composite anode and pair with a Na metal anode and we design  $\text{Na}||\text{Na-CNF}$  cells to test the electrochemical performance and stability of the composite anodes (Figures 5.5b,c). The cells are cycled for a total areal capacity of  $0.5 \text{ mAh cm}^{-2}$  at a current density of  $0.5 \text{ mA cm}^{-2}$  and we measure the time that the cells begin to have a rapid

increase in the cell's overpotential and signal the time of failure, or active metal consumption, on the composite anode. For the  $\text{NaPF}_6$  containing electrolytes, the P:B 80:20 composite anode is the first to undergo the rapid increase in overpotential at 228 hours, followed by the pure  $\text{NaPF}_6$  anode at 314 hours, P:D:B 90:5:5 at 350 hours, and P:D 80:20 at 450 hours. For the  $\text{NaBF}_4$ , D:B 75:25, and NaDFOB composite anodes, the  $\text{NaBF}_4$  cell shorts after only 8 hours, while the D:B 75:25 cell increases at 480 hours and the NaDFOB cell at 916 hours. The heavily oxidized Na metal on the composite anode suggests that the active Na metal is almost entirely consumed during electrodeposition and is unable to effectively cycle. Overall, the inclusion of the  $\text{NaBF}_4$  decreases the stability of the electrodeposited Na metal, while NaDFOB enhances the composite anode's stability and improves its cycling capability.

While  $\text{NaPF}_6$  has a higher conductivity and high oxidation potential, it does not have good electrochemical stability for long-term cycling. The  $\text{NaPF}_6$  salt is easily reduced against the Na metal anode, has poor thermal stability, and produces an insufficient and unstable SEI for preventing dendrite formation or effectively protecting the Na metal anode from continuous side reactions. Meanwhile, throughout our investigation, we observe that the NaDFOB containing electrolytes have an enhanced cycle life, reduced impedance in the cell, and a more robust SEI on the Na metal anode surface. The inclusion of NaDFOB improves overall stability and performance in the Na cells.

## 5.4 Conclusion

In summary, we measured the electrochemical properties and performance of a range of electrolyte formulations and probed the anode-electrolyte interfacial chemistry of our selected electrolytes and the Na metal anode. We revealed the inefficiencies of NaPF<sub>6</sub> and NaBF<sub>4</sub> as sufficient salts for stable long-term performance and highlighted the beneficial aspects of NaDFOB as a primary, or as an auxiliary salt against Na metal anode. The small ESW and poor conductivity of the NaBF<sub>4</sub> electrolyte had a detrimental effect on the electrochemical stability and performance of the electrolytes that contained NaBF<sub>4</sub>. With NaDFOB in the electrolyte, we observed enhanced cycle life of the Na||Na symmetric cells, a reduced cell impedance, a highly stable SEI, and improved cycling capabilities for “lean” Na composite anodes. The oligomerization of the DFOB anion formed a more robust and capable SEI and protected the Na metal anode from early-onset dendrite formation and excessive side reactions. Further analysis of electrolyte engineering will be necessary to understand the electrolyte’s compatibility with the Na metal anode and to further optimize the composition of the electrolyte for more desirable anode-electrolyte interactions and improving the electrolyte’s stability and electrochemical properties.

## 5.5 Experimental Section

### 5.5.1 Materials Synthesis

Electrolyte formulations were calculated for a total of 1 M concentration (w:w ratios) and dissolved in PC solvent. NaDFOB was synthesized through the reaction of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (Sigma-Aldrich) and BF<sub>3</sub>·ether (Sigma Aldrich) in acetonitrile, which has been described in ref 39. NaPF<sub>6</sub> and NaBF<sub>4</sub> were obtained from Sigma Aldrich (98%).

### 5.5.2 Materials Characterization

XPS characterization was performed on a PHI VersaProbe III scanning XPS microscope using monochromatic Al K-alpha X-ray source (1486.6 eV). Samples were transferred from an Ar-filled glove box to the XPS ultrahigh vacuum chamber via a vacuum transfer vessel. All binding energies were referenced to C-C peak at 284.8 eV.

### 5.5.3 Electrochemical Characterization

CR2032 coin-cells were assembled in an Ar-filled glovebox with the 1 M electrolytes in PC solvent. The Na symmetric cells were made with Na metal foil discs with glass fiber separator and the volume of the electrolyte was in excess. The Na-CNF composite anode was prepared with an adhered pristine CNF disc ( $2\text{ cm}^2$ ) to a copper current collector as the positive electrode and an Na foil disc ( $1.13\text{ cm}^2$ ) as the negative electrode in a coin cell. The current density used for electrodeposition was  $0.25\text{ mA cm}^{-2}$  for a total areal capacity of  $3\text{ mAh cm}^{-2}$ . All coin cells were assembled in an Ar-filled glovebox. LANDT and MACCOR battery testers and software were utilized to collect all Na cell cycling data. Electrochemical impedance spectroscopy and ionic conductivity measurements were performed on a Princeton Applied Research VersaSTAT.

## 5.6 Acknowledgements

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## 5.7 Supporting Information

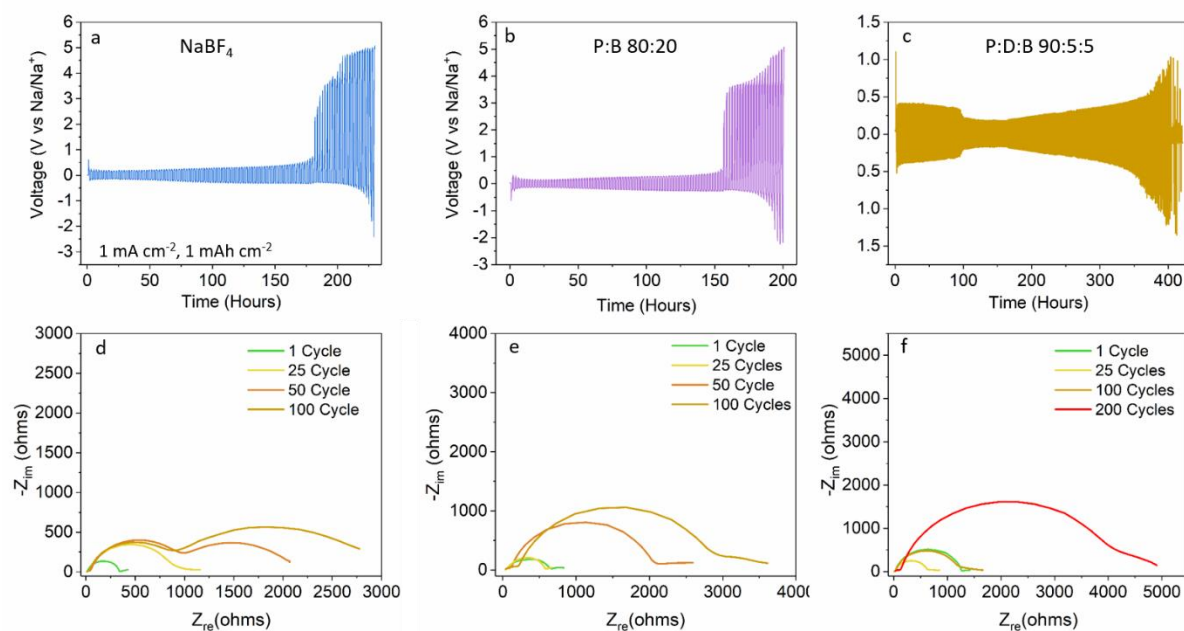


**Figure S5.1)** Galvanostatic cycling results from symmetric Na-Na cells cycled at a current density of 1 mA cm<sup>-2</sup> with an areal capacity of 1 mAh cm<sup>-2</sup> for a) NaBF<sub>4</sub>, b) P:B 80:20, c) P:D:B 90:5:5 electrolytes. Electrochemical impedance spectroscopy for symmetric Na-Na cells measured during cycling for d) NaBF<sub>4</sub>, e) P:B 80:20, f) P:D:B 90:5:5.

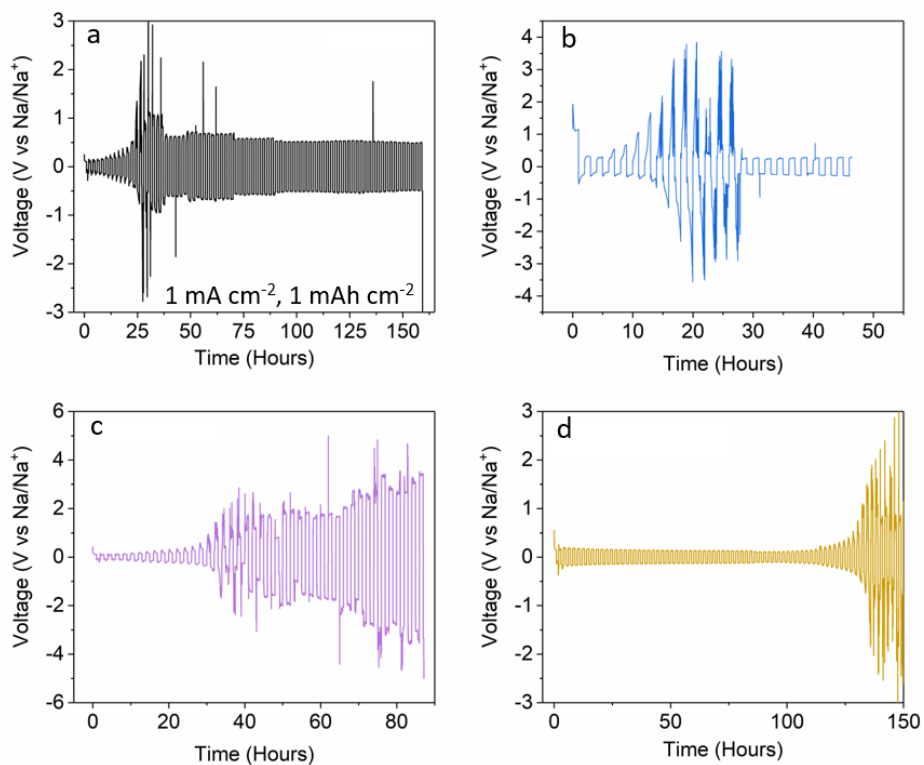


**Figure S5.2)** Elevated temperature galvanostatic cycling results from symmetric Na-Na cells cycled 45°C for a)  $\text{NaPF}_6$ , b)  $\text{NaBF}_4$ , c) P:B 80:20, and d) P:D:B 90:5:5 electrolytes at a current density and areal capacity of  $1 \text{ mA cm}^{-2}$  and  $1 \text{ mAh cm}^{-1}$ .

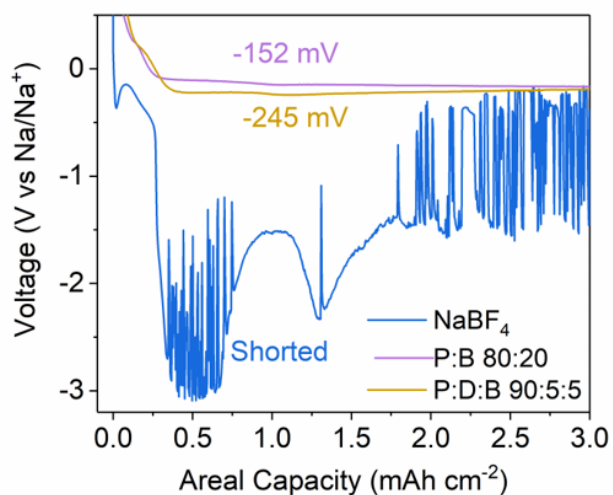


**Figure S5.3)** Electrodeposition profile for  $\text{NaBF}_4$ , P:B 80:20, and P:D:B 90:5:5 electrolytes with the overpotential required to begin the Na metal nucleation phase onto the CNF substrate.

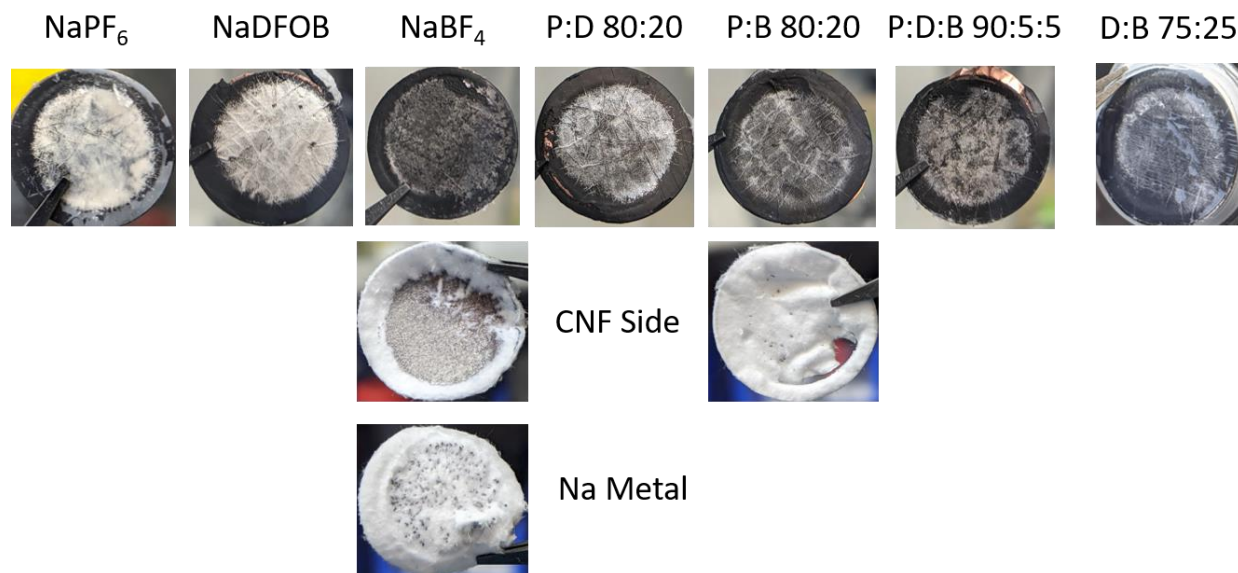


**Figure S5.4)** Photographs of the surface of the Na-CNF composite electrodes after 3 mAh cm<sup>-2</sup> Na metal electrodeposition with each electrolyte composition. Separators from cells using NaBF<sub>4</sub> and P:B 80:20 electrolytes after electrodeposition showing dead Na electrodeposited on the CNF (positive) and Na metal (negative) electrode side of the coin cell.

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## 6. Conclusions and future work

### 6.1 Conclusions

This dissertation mainly focused on two aspects: the interfacial interactions of the alkali metal ion and the carbon nanofiber host material and the electrode-electrolyte interfacial chemistry via electrolyte engineering utilizing sodium borate salts.

We first begin our investigation on the design of “lean” alkali metal-carbon composite anodes. Li metal is electrodeposited onto an amorphous carbon nanofiber (CNF) substrate with a range of total areal capacities of lithium loading ( $1\text{-}3\text{ mAh cm}^{-2}$ ). The effect of the loading of Li metal, the electrolyte composition, and current density used during electrodeposition had on the electrochemical performance of the “lean” Li-CNF composite anode was measured. Electrochemical cycling revealed that the addition of vinylene carbonate (VC), of 2% (w:w), improved the cycle life of the Li-CNF anode, and that increasing the electrodeposition current density resulted in heterogenous Li plating and reduced the cycle life of the composite anode. The utilization of a graphite electrode as a substrate for Li electrodeposition significantly improved the cycling capabilities of the “lean” composite anode. Increasing the crystallinity of the substrate can improve the longevity of “lean” composite anodes through enhanced  $\pi$ -bond–p orbital interactions between the graphite interlayers and Li ions. The results highlight the possibility of enabling “lean” composite anodes through optimizing the crystallinity of the carbon substrate and electrolyte engineering.

In chapter 3, a semi-crystalline CNF substrate was prepared and used to investigate the interfacial ion-host interactions of Li and Na metal with the structural characteristics of the CNF substrate to enable a dual mechanism hybrid ion/metal composite anode. The crystallinity and

structure of the CNF was found to be more comparable to a hard carbon material. The Na-CNF composite anode had improved electrochemical performance and stability over the Li-CNF anode. Electrochemical ion kinetic analysis revealed that Na ions intercalated into the crystalline interlayers, while Li ion was limited to surface adsorption. The intercalation of Na ion significantly enhanced the electrochemical cycling longevity of the composite anode. However, the stability of the actual electrodeposited Na metal was much poorer than the electrodeposited Li metal. Improving the stability of electrodeposited Na metal has two main pathways: further optimization of the CNF substrate, through continued optimization of the crystallinity and/or modifying the surface functionalization, or through electrolyte engineering to reduce undesired reactions during the electrodeposition process and improving the anode-electrolyte interfacial chemistry.

The utilization of sodium borate salts in sodium electrolytes was investigated to improve the electrode-electrolyte interfacial chemistries in Na batteries. In chapter 4, the cathode-electrolyte interfacial interactions were probed through electrolyte modification of multi-salt electrolyte formulations at various temperatures. The use of sodium difluoro(oxolato)borate (NaDFOB) as a primary, or as an auxiliary salt, significantly improved the stability of the  $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NFM 333) cathode through the formation of a robust cathode-electrolyte interphase (CEI). The more capable CEI bolstered a suppression of transition metal oxide (TMO) reduction in the surface and bulk of the cathode particles, mitigation of TM dissolution from the surface of the cathode, and minimization of cathode particle degradation and nanocrack formation.

In chapter 5, the electrochemical properties of the previously selected electrolyte compositions were measured, and the anode-electrolyte interfacial and electrochemical properties were investigated. The NaDFOB containing electrolytes were found to have a more robust solid electrolyte interphase (SEI), lower cell impedance, and improved electrochemical performance

against Na metal anode at room and elevated temperatures. “Lean” Na-CNF composite anodes were developed with the selected electrolytes. The electrodeposited Na metal in the pure NaDFOB electrolyte had the most pristine metallic color and most stable electrochemical performance. The NaDFOB containing electrolytes reduced undesired side reactions and improved the stability of Na metal and has promising potential for further investigation for Na battery applications.

## **6.2 Perspective of future work**

### **6.2.1 The optimization of carbon substrate crystallinity and functionalization**

The study of utilizing a semi-crystalline CNF substrate for “lean” alkali metal composite anodes (Chapter 3) revealed that the crystallinity improved the alkali metal ions with the CNF substrate<sup>1–3</sup> and improved the cycling performance of the composite anodes. However, the requirements for alkali metal ion for intercalation within the CNF interlayers is different. A systematic study of the graphitization temperature parameters to control the content of crystallinity and d-spacing of the graphitic interlayers should be investigated. Once the optimal CNF crystallinity is obtained, a study of enhancing the lithio- and sodiophilicity of the CNF to improve the interfacial interactions to improve the local charge homogeneity along the CNF and reduce the binding energy required for Li and Na metal nucleation and plating. Two methods for this approach can be achieved is through heteroatom doping on the CNF surface with O, N, B, etc. species to improve the Li or Na binding affinity to the CNF surface.<sup>1–3</sup> Another approach is doping the CNF surface with metal atoms to improve the alkali metal affinity to the substrate.<sup>4,5</sup>

### 6.2.2 Further investigation of cathode particle stabilization

The incorporation of sodium borate salts significantly improved the passivation and stability of the Na cathode particles and suppression of TM dissolution (Chapter 4). However, further investigation into the stability of the cathode particles should be performed. A substitution method using a cation that has stronger binding with the oxygen anions in TMO cathode lattice can be utilized to inhibit oxygen loss from the particle surface. Metal cations such as Ti, Mg, Al, etc. have been used in Li cathodes to suppress the TM-O hybridization that can promote oxygen release from the lattice and cause irreversible surface reconstruction and TM dissolution.<sup>6–9</sup> Therefore, combining the cathode stabilization through TM substitution with more effective passivation of the NaDFOB electrolytes should be investigated.

### 6.2.3. Further probing electrode-electrolyte interfacial chemistry

The work in Chapters 4 and 5 lays the groundwork for investigating the electrode-electrolyte interfacial chemistry for sodium TMO cathodes and Na metal anode. The electrolyte compositions investigated included a broad range of composition ratios to determine a general direction for electrolyte design. Further optimization of the electrolyte ratios for select electrolyte combinations should be pursued. In continuing the study, other well researched electrolyte salts and solvents should be considered for improving the electrode-electrolyte interface and electrode passivation. Furthermore, analytical techniques such as NMR, synchrotron X-ray photoelectron spectroscopy (XPS), and cryo-transmission electron microscopy can serve as powerful tools for high resolution probing of the compositional and structural information, and the kinetic characteristics of the electrode-electrolyte interfacial chemistries of the cathode and anode.<sup>10–13</sup>

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