

ABSTRACT

Title of Dissertation: NEXT GENERATION ANODES FOR
LITHIUM ION AND LITHIUM METAL
BATTERIES

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Engineering of specific battery components can yield incremental gains in performance, but sustained advancements are derived from an understanding of charge transfer, interphase formation, and ion storage in the system. In this dissertation, the next generation of lithium-ion and alkali metal anodes are integrated with promising flame retardant electrolyte systems for safe and energy-dense portable storage devices. The intent of this research is to bring safe lithium ion batteries to the market without compromising performance and, more specifically, volumetric energy density.

The first part of this dissertation describes the invention and optimization of a silicon-based additive which employs a solution-based process to functionalize silicon nanoparticle precursors. The additive is thoroughly characterized by chemical and electrochemical methods and the electrolyte interphase is improved by the attachment of partially reduced graphene oxide and sacrificial additive species. The design principles developed for the silicon-based system deviate significantly from those used for other conventional intercalation and host electrodes. As a result, in the second part

of this dissertation, three chemically separable electrolyte systems, selected for their flame retardant properties, are individually investigated and tailored for energy-dense pouch cells. The bulk transport and interfacial properties of each electrolyte system are adapted to meet the industry standards of portable electronic devices. Insights into the preferred species for stable solid electrolyte interphase formation are discussed with an emphasis on the impact of fluorinated solvents and sacrificial additives. In the last part of this dissertation, alkali metal hosts are also proposed for chemistries beyond lithium ion. Novel synthesis methods including rapid joule heating are explored to form the innovative host architectures which greatly mitigate the coulombic inefficiency of metal stripping and plating in half and full cell configurations. The design principles outlined in this dissertation reveal how to successfully engineer the charge transfer, interphase formation, and ion storage of high capacity electrodes with safe electrolyte for state-of-the-art portable energy storage devices.

NEXT GENERATION ANODES FOR LITHIUM ION AND
LITHIUM METAL BATTERIES

by

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List of Abbreviations

CB	Carbon black additive
CC	Constant current and constant current protocol
CE	Coulombic efficiency ($Q_{n,oxidation}/Q_{n,reduction}$)
CIE	Coulombic inefficiency (1-CE)
CNF	Carbon nanofiber
CNT	Carbon nanotube
CVD	Chemical vapor deposition
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
dQ dV ⁻¹	Differential capacity analysis
DOD	Depth-of-discharge
EC	Ethylene carbonate
EDS	Energy dispersive X-ray spectroscopy
FEC	Flouroethylene carbonate
FTIR	Fourier transform infrared spectroscopy
Gr	Graphite
HFE	1,1,2,2-tetrafluoroethyl-2',2'-trifluorosthyl ether
HGCNF	Hollow graphitic carbon nanofiber
ICE	Initial Coulombic efficiency ($Q_{1,oxidation}/Q_{1,reduction}$)
LCO	Lithium Cobalt Oxide
LCV	Lower cutoff voltage
LFP	Lithium iron phosphate
LIB	Lithium-ion battery
LiDFOB	Lithium difluorooxalatoborate
LiFSI	Lithium bis(fluorosulfonyl)imide
LiNO ₃	Lithium nitrate
LiPF ₆	Lithium hexafluorophosphate
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
MIL	Mixed ionic liquid
NMC	Lithium nickel manganese cobalt oxide
OCV	Open circuit voltage
PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile
pRGO	partially reduced graphene oxide
PYR ₁₃ TFSI	N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
ROI	Region of interest
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SOC	State-of-charge
TEM	Transmission electron microscopy
UCV	Upper cutoff voltage
VC	Vinylene carbonate

Chapter 1: Introduction

1.1. State-of-the-art Lithium Ion Batteries

Experimental electroactive materials for lithium-ion batteries (LIBs) are largely limited by structural instabilities and undesirable secondary faradaic reactions. As a result, mature materials that offer greater stability with reliable electrochemical performance, such as graphite (Gr) and lithium cobalt oxide (LCO), have been difficult to displace. However, these mature battery chemistries have been pushed to their theoretical limits and will restrict further growth and adoption of technologies dependent on portable energy storage. In particular, the future incorporation of intermittent renewable energy sources and disruptive technologies, such as electric vehicles and portable electronics, is closely tied to the development of better energy storage solutions.¹ LCO||Gr full cells (n/p ratio = 1.285) developed by Argonne's Cell Analysis, Modeling, and Prototyping (CAMP) facility have a theoretical energy density of 676 Wh L⁻¹, excluding all electrochemically inactive material. This is already ~5% lower than the volumetric energy density of 2170 cells used in today's Tesla vehicles (711 Wh L⁻¹), which includes the packaging and inactive cell components.² Therefore, the push to design and implement novel electroactive materials stems from a tangible commercial demand and requires economical solutions.³

The discovery of the Li-Si alloy as an anode material in the 1970s, with a high theoretical capacity (3579 mAh g⁻¹ as Li₁₄Si₅), sparked a plethora of novel and exciting designs for alloying-based negative electrodes.⁴ Compared to other alloying-based materials, Si provides not only a high theoretical capacity in its lithiated state, but it is also widely abundant, volumetrically and gravimetrically dense, and discharges at an advantageous potential to pair with lithium oxide-based

cathodes (0.4 V versus Li/Li+). However, even after decades of pointed research,^{5–17} the large volume expansion of the alloying reaction and unstable solid electrolyte interphase (SEI) formation cripple the performance of economical Si-based negative electrodes.¹⁸ Furthermore, it is still difficult to pin down how various cell parameters and cycling conditions impact the cycling performance of Si electrodes.¹⁹ In particular, some of the most challenging hurdles related to Si electrode performance in full cell configurations, namely electrode swelling and capacity fade, have been largely overlooked by past studies.^{20,21}

The theoretical gravimetric specific capacity of electroactive materials can be predicted by Faraday's law below.

$$m = \frac{QM}{Fz} \rightarrow \frac{Q}{m} = \frac{Fz}{M} \quad (1.1.1)$$

where m is the mass of the substance at the electrode (g), Q is the capacity or total electric charge passed through the substance (C), $F = 96485 \text{ C mol}^{-1} = 26801 \text{ mAh mol}^{-1}$, M is the molar mass of the substance (g mol^{-1}), z is the valency of the ionized substance. Using this equation, and from experimental studies on the observed lithiation of silicon, it is possible to construct Table 1.1.^{22–26} Even after disregarding the infrequently observed the $\text{Li}_{22}\text{Si}_5$ state, the values associated with the metastable $\text{Li}_{15}\text{Si}_4$ state are enormous compared to topotactic negative electrode materials such as graphite or lithium titanate (LTO). Therefore, Si-containing electrodes and full cells need to be engineered to handle the significant stressed associated with coulombic efficiency without sacrificing capacity or energy density.

Table 1.1. Properties of the lithiated states of silicon. Gravimetric specific capacity is calculated using Faraday's law, Equation 1.1.1.²⁷

Lithiated States of Silicon	Silicon Atom Volume ($\text{\AA}^3$)	Volume Expansion (%)	Gravimetric Specific Capacity (mAh g^{-1})	Volumetric Specific Capacity (mAh cm^{-3})
Si	19.6	0	0	0
LiSi	31.4	60	954	1389
$\text{Li}_{12}\text{Si}_7$	43.5	122	1636	1716
Li_2Si	51	160	1909	1710
$\text{Li}_{14}\text{Si}_6$	51.5	163	2227	1972
$\text{Li}_{13}\text{Si}_4$	67.3	247	3101	2082
$\text{Li}_{15}\text{Si}_4$	76.4	290	3579	2137
$\text{Li}_{22}\text{Si}_5$	82.4	320	4199	2328

The most successful engineering approaches for highly reversible Si-containing negative electrodes can be split into four categories, with some overlap: (i) coatings and artificial interphase layers (aSEI),^{5,8,15,28–34} (ii) architectures and structures,^{35,21,36–43} (iii) alloys,^{20,44–48} and (iv) binders.^{14,49–56} In this dissertation, a graphene oxide coating, high mass loading composite architectures, and engineered aqueous binders are reported to improve the coulombic efficiency of Si-containing electrodes. High capacity and energy dense full cells are also described after pairing with various positive electrodes.

Lithium nickel manganese cobalt oxide (NMC) positive electrodes suffer from a battery of independent and coupled issues in full cell configurations with Si-based negative electrodes. Recent work has focused primarily on enhancing the cycling and structural stability of NMC through interface engineering methods.^{57–60} However, much of this work pertains strictly to half-cell configurations with lithium metal reference electrodes or graphite negative electrodes. Configurations with silicon based negative electrodes are more complicated due to cross-talk

between electroactive materials which introduces novel challenges in electrolyte and electrode design. Enhancing the stability of these materials through practical electrode designs and electrolyte formations will hopefully enable the next generation of high energy density LIBs. In this dissertation, both 532 and 811 NMC stoichiometries are investigated for energy dense full cells. The performance of the full cells is found to depend largely on the bulk and interfacial properties of the system, which are largely shaped by the electrolyte.

Electrolyte systems are responsible for ion conduction between the positive and negative electrodes in galvanostatic and electrolytic cells. In lithium ion batteries, the electrolyte is conventionally comprised of a lithium-based salt, generally lithium hexafluorophosphate, and a mixture of aprotic, carbonate solvents, such as ethylene carbonate (EC) and ethyl methyl carbonate (EMC), diethyl carbonate (DEC), or dimethyl carbonate (DMC). These components determine the bulk transport properties.

In aprotic systems, when a Li salt is dissolved into a blend of solvents, it dissociates into its constituent cation and anion components. The dissociation of the salt and the formation of a solvent shield are strongly related to the molecular structure of every species in the system, as well as the dielectric constant of the solvents. Li salts with larger, electron-rich anions are better at distributing their charge which deters ion pairing, improves solubility, and typically improves ionic conductivity. While smaller anions from salts, such as LiF and LiCl, have low solubility in nonaqueous solvents and therefore poor ionic conductivity.⁶² In this dissertation, the commercial standard LiPF₆ is tested against other Li salts such as LiTFSI, LiFSI and LiDFOB to improve the bulk transport and interfacial properties of NMC||Si-based full cells. The results are reported throughout Chapter 4.

Solvents with a higher dielectric permittivity can better solvate Li^+ cations, sheath the cations from the anion, and thereby thoroughly dissociate the conductive salt. Furthermore, a high viscosity eases the transport of dissociated cations to either electrode while cycling. Few solvents boast both a high dielectric constant and high viscosity for lithium ion electrolyte systems. Therefore, in this dissertation, multi-solvent systems are investigated so that various solvents contribute separate properties to the bulk transport properties. In commercial lithium ion batteries, EC, with a high dielectric permittivity of 89.6, dissociates the Li salt and forms a stable interface on graphitic anodes to prevent solvent intercalation and layer exfoliation. However, EC is a solid at room temperature and therefore must be mixed with one or more carboxylic esters or acyclic carbonates to function at room temperature with 5 - 10 mS/cm ionic conductivity.⁶³ In the work reported in the subsequent chapters, EC and fluorinated EC (also known as FEC) are tested and characterized with various solvents with higher viscosity. Other EC-free systems with ionic liquids, sulfones, and fluorinated solvents are also investigated which can provide better thermal stability and interphase stability in NMC||Si-based systems.

The simplified transport properties associated with electrolyte systems can be expressed by the transport number (Equation 1.1.2), where $i_{\pm}$ is the current, $u_{\pm}$ is the mobility, and $D_{\pm}$ is the diffusion coefficients of the cations and anions, respectively. However, this metric does not consider coulombic drag during ion conduction from the solvent shield or counterion, needed to maintain global charge neutrality. Therefore, the transport number is only pertinent to dilute systems with DC polarization < 10 mV. Drag is considered by the transference number (Equation 1.1.3), which quantifies the fraction of useful Li cation migration from the total electric current, where ΔV is the polarization voltage, $I(\infty)$ is the steady-state current, R_b is the bulk resistance, and R_{ct} is the charge transfer resistance.⁶¹ A higher transference number indicates less

concentration polarization while cycling, however commercial LIB electrolyte have a transference number around 0.3.

$$t^+ = \frac{i_+}{i_+ + i_-} = \frac{u_+}{u_+ + u_-} = \frac{D_+}{D_+ + D_-} \quad (1.1.2)$$

$$T_{Li^+}^+ = \frac{R_b}{\Delta V / I(\infty) + R_{ct}} \quad (1.1.3)$$

Commercial electrolyte systems are also carefully tuned through the addition of low weight percent additives to impart desirable interfacial properties for the anticipated use conditions and environment. Novel electrolyte systems must therefore be comparable to or provide overwhelming benefit in one of the following metrics: price, toxicity, ionic conductivity within the temperature range of interest, wettability, viscosity, anodic and cathodic stability, interphase formation, interphase stability, ion association and ion-solvent interactions, solvation, salt concentration, parasitic reactions, and safety.⁶¹ In this dissertation several promising additive packages are discussed in novel and conventional solvent mixtures. Many of the systems are specifically designed with flame retardant components and properties. This is an elusive but extremely appealing property for numerous portable energy applications which have been plagued by catastrophic incidents due to flammable carbonate systems. However, rarely can performance be compromised by improved safety over the commercial standard. Therefore, much of the work prioritizes battery systems with energy dense electrodes and flame retardant electrolyte.

1.2. High-temperature Synthesis of Energy Storage Materials

Nanoengineering offers versatile solutions and methods for a broad array of energy storage and catalysis applications.^{66–69} However, the limited scalability and prohibitive costs associated with etching and post-treatment processes has impeded the incorporation of nanoengineering in large-scale battery systems. Conventional heat treatment processes for nanoparticles are reluctantly implemented despite long processing times with highly reactive and unstable precursors. The thermal stability of nanoparticles is such that decomposing, welding, or forming particles from precursors can be conducted at lower temperatures in inert atmospheres. However, challenges persist to maintain the precise phase and uniform size distribution by industrial scale methods. Alternative techniques such as joule heating offer benefits such as fast processing times and unique morphologies that are still being explored for nanoparticle formation.^{70–72} Unlike heat treatment processes in a furnace that operate by convection, heating by conduction can be optimized to conserve energy with accelerated particle formation.

The Hu group has pioneered research on energy storage materials synthesized by rapid Joule heating in an inert atmosphere. This dissertation report on synthesizing both catalyst and energy storage materials by the novel high temperature electrical pulse technique.^{70,71,73–75} In particular, experiments focused on creating novel structures such as hollow graphitic carbon nanofibers and metal decorated nanofibers are described. Hollow graphitic carbon nanofibers (HGCNFs) constitute a unique class of nanocarbons due to their distinctive one-dimensional (1D) structure with high surface area, high structural and thermal stability, as well as high electric and thermal conductivity. These materials are appealing for niche applications including catalyst and sensor supports, hydrogen storage materials, gas storage,⁷⁶ and electrochemical devices,^{77–79} however fabrication by conventional methods is both arduous and uneconomical. More

specifically, methods such as chemical vapor deposition (CVD), hydrothermal processes, and template-based depositions have been adapted for the synthesis of HGCNFs but lack commercial viability.⁸⁰ Synthesis of porous graphitic carbon nanofibers (CNFs) and carbon nanotubes (CNTs) has been previously reported by the decomposition of various gasses, such as methane or acetylene, on transition metal nanocrystals (e.g. Ni, Co, Fe, etc.). Additionally, hydrothermal methods using Te nanowires as preferred nucleation sites also achieved 1D CNFs and porous CNTs with excellent rate capability for lithium ion negative electrodes.⁸¹ However, by CVD or the hydrothermal method, it can be challenging to control the porosity and diameter of the resulting nanocarbon materials. Nanostructured carbon prepared by the hydrothermal method also has a low degree of graphitization, giving rise to undesirably low conductivity. Electrospinning polymer precursor solutions with single, coaxial, or triple coaxial nozzles can form various promising CNFs morphologies after curing or annealing. This method is scalable but requires extended high temperature processes which can be improved through novel methods. Recent research on hollow 1D carbon nanostructures shows excellent performance in electronic devices, supercapacitors, and lithium-based batteries, but synthesis strategies need to be optimized to commercialize unique nanocarbons. The interconnected carbon network formed by CTS of polyacrylonitrile-based carbon nanofibers at a high temperature (> 2000 K) and ultra-fast rate (up to 10^4 K min⁻¹) is reported. The ephemeral high temperature environment enables carbonization and dilation of the nanofibers to form a 3D hollow carbon network without significantly altering the structural integrity of the film. The process and characterization of these new materials will be thoroughly discussed to clearly delineate the CTS process from conventional annealing processes.⁷⁷

Chapter 2: Research Objectives

Despite the wealth of effort directed at high energy density negative electrodes, carbon remains the element of choice for portable and rechargeable energy storage. Thus, the purpose of this work is to increase the (i) volumetric energy density, (ii) capacity retention, and (iii) rate performance of previously developed LIB technologies by designing novel high-capacity systems. The objectives are split between three approaches: the development of (i) novel Si-based electrodes which can be easily substituted into current LIB systems, (ii) nonflammable electrolyte with tailored SEI formation for NMC532||SiGr full cells, and (iii) the synthesis of novel alkali metal hosts for lithium metal electrodes.

Chapter 3 begins with a review of the most pertinent reports of silicon-based electrodes for commercial lithium ion batteries. Section 3.1 describes a novel synthesis process for scalable negative electrodes. The work demonstrates improved performance by functionalizing and coating Si nanoparticles with amine groups and partially reduced graphene oxide, respectively. The morphology and properties of the Si additive and resultant negative electrodes are described in Section 3.2. This work was reported and accepted as a provisional patent (PS-2018-0101) to the University of Maryland patent office. Half and full cell performance of the novel negative electrode paired with NMC cathodes is given in Section 3.3. In isolated half-cell measurements, the highly conductive and amine-functionalized negative electrode demonstrates enhanced stability with > 90% initial coulombic efficiency (ICE) at 1394 mAh g⁻¹ and > 99.0% efficiency during subsequent activation cycles. Recently, major battery manufacturers have gradually incorporated low Si loading composite electrodes (5 - 15%) into state of the art cells, due to the overall reduction in LIB cost and increase in energy density.⁸² In these cases, the capacity contribution from graphite in these electrodes still outweighs that from electroactive silicon. The

electrodes reported in Section 3.3 contain 30 wt% of Si additive and, as a result, graphite contributes only 17% to the total theoretical capacity of the negative electrode (215 mAh g⁻¹ out of 1289 mAh g⁻¹ overall). This configuration is widely recognized as one of the most promising chemistries for reducing the cost and increasing the energy density of lithium ion batteries.

Electrode architectures that result in low mass loading or high porosity defer rather than solve the most fundamental challenges associated with high capacity materials. In the work presented in Section 3.4, high mass loading ($> 4.5 \text{ mg cm}^{-2}$) negative electrodes with 30 wt% of Si additive and high mass loading ($\leq 60 \text{ mg cm}^{-2}$) LFP positive electrodes are demonstrated in half cells to compare with lower mass loading batches. An active material synthesis requiring highly corrosive acid (HF) or high temperature annealing are avoided to accelerate processing of the drop-in Si additive and LFP cathode.^{83,84} In particular, enhancements to the stability and design of silicon-based electrodes through core-shell or other interface formers are avoided due to cost constraints.

Cell metrics such as the cell thickness, coulombic efficiency, resistance, voltage, and capacity are readily obtainable from simple electrochemical and mechanical measurements. However, these measurements provide minimal insight into the degradation mechanisms and SEI formation of the respective electrode. As a result, methods including post-mortem analysis, chemical species analysis, electrochemical analysis, and in-situ measurements are crucial to understanding how to integrate silicon electrodes into practical LIB designs [References]. Section 3.5 includes discussion of how the lower (LCV) and upper cutoff voltages (UCV) of silicon-based full cells impact performance through differential capacity analysis (dQ dV⁻¹). These experiments reveal the importance of voltage window optimization on a per system basis. Previous works by Dahn's group⁸⁵⁻⁸⁸ have similarly demonstrated the use of differential capacity analysis on LCO||Gr

full cells as a quality assurance tool while other groups^{20,45,89} have emphasized the importance of cutoff voltages in silicon-based configurations.

The design and characterization of novel aqueous binders for silicon-based electrodes is described in Section 3.6. First, the selection criteria for binders in Si-based binders is briefly outlined and the mechanism of an archetypical binder first proposed by Yushin's group, polyacrylic acid (PAA), is given.⁵⁶ Then, experiments to test a series of binary binder blends with the composition $x\text{PAA};y\text{SBR}$ are detailed and the results are discussed. The optimized binary blend is found to have superior mechanical and electrochemical performance to either single-phase constituent. By mixing a hard and soft binder together, a hard and tough binder is realized of Si-based electrodes. Further work on this top is being pursued by my colleague, Miaolun Jiao with more promising polymers which offer better hydrogen bonding for self-healing properties.

The fabrication of ultrathin and flexible LFP||Gr pouch cells is described in Section 3.7. A novel packaging solution is specifically developed for wearable and IoT applications using heat-sealable polyimide substrates. Current collectors and other inactive battery components are minimized in the novel packaging design by redesigning and integrating components together. Long-term cycling tests of the LFP||Gr chemistry are discussed and the performance is compared to the high-capacity Si-based electrodes from the previous sections. Bending videos are included in the supplemental information.

In Chapter 4, various electrolyte systems are studied in full cell configurations with Si composite negative electrodes to overcome the challenges associated with excessive decay and safety in high energy density lithium ion batteries. Commercial organic electrolyte consists of a lithium salt dissolved in some combination of non-aqueous solvents with high dielectric permittivity or low viscosity at room temperature. In batteries with a lithium metal oxide cathode

and graphitic anode, lithium hexafluorophosphate (LiPF_6) is the most common salt due to its cost, self-passivation on Al, chemical stability, and transport properties. Although it is not necessarily ideal, it performs adequately without significantly reducing the safety or cost of the final battery system.^{62,63} In most commercial cells, ethylene carbonate (EC) is a necessity to dissociate the Li salt due to its high dielectric permittivity and establish a unique passivating layer, known as SEI, on graphitic carbons. However, ethylene carbonate cannot act as the sole solvent in the battery system because of its high melting point (34 - 37 °C). Linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylmethyl carbonate (EMC) can mix with EC and provide low viscosity at room temperature to better dissociate the salt in the electrolyte in solution, thereby improving ionic conductivity and enabling room temperature functionality.^{63,90} As a result, the baseline electrolyte system throughout this dissertation is 1.0 M LiPF_6 in EC:DEC (50:50 ratio by weight). This electrolyte is flammable and therefore susceptible to catastrophic failure from demanding loads and various extreme environments. A key target from this work is to develop an electrolyte system less prone to exothermic electrolyte breakdown without sacrificing performance.

Section 4.1 describes the development of a mixed ionic liquid electrolyte and gel membrane with reduced flammability for energy dense configurations. Room-temperature ionic liquids with high thermal stability, high ionic conductivity, and high voltage stability are promising electrolyte for extreme battery applications. The standard properties of ionic liquids are discussed in the context of room-temperature electrolyte systems. In this dissertation, the performance of mixed ionic liquid batteries are optimized and investigated for flexible and high-capacity energy storage solutions. In particular, optimization for silicon-based configurations is thoroughly discussed and challenges associated with the Si SEI are identified. Stringent tests to improve the

PVDF-based electrolyte printing process and check the safety of the gel electrolyte are also described. While mixed ionic liquid systems can show greater thermal stability than the baseline organic system, they do not completely resolve the concerns related to exothermic electrolyte breakdown.

Nonflammable sulfonate-based electrolyte systems that are inherently safe and insusceptible to catastrophic failure are briefly discussed in Section 4.2. However, these systems are found to be unsuitable for full cell configurations with layered metal oxide cathodes and silicon-based anodes. Sulfonates had been previously demonstrated in olivine type cathodes with purely graphitic anodes. The present work reveals issues associated with wetting of polymer-based separators and excessive SEI formation with alloying-based electrodes which significantly hinder electrochemical performance. Fluorinated ethers demonstrate flame-retardant properties in battery systems while minimally impacting electrochemical performance including anodic stability, electrolyte conductivity, and SEI formation. In particular, 1,1,2,2-tetrafluoroethyl-2',2',2'-trifluoroethyl ether (HFE) acts as a diluent in lithium ion systems which rarely solvates due to its low permittivity or donates charged species to directly impact electrochemical transport. As a result, in Sections 4.2 and 4.3, flame retardant systems using HFE are reported with appealing performance in high-capacity battery systems.

Section 4.3 further elaborates on the optimization of a flame retardant system for energy dense batteries and details the systematic search and characterization of electrolyte additives. Electrolyte additives are notoriously challenging to deliberately design and anticipate for lithium ion batteries. This struggle stems from a lack of understanding of SEI formation and chemistry. A growing number of additives have been developed and reported for numerous systems. One of the main challenges with developing a new battery system is the re-evaluation of additives that may

have been previously known and investigated. In this study, additives for NMC||Si-Gr full cell configurations are first reviewed from the literature and then systematically investigated. As such, the most important additive for silicon-based electrodes, historically, has been fluorinated ethylene carbonate (FEC). This material helps to form a thinner SEI than its non-fluorinated counterpart by preferentially reducing (LUMO energy: 0.98 eV vs. 1.17 eV for EC)⁹¹ on the negative electrode.

Chapter 5 consists of experiments to synthesize alkali metal hosts for Li metal electrodes with similar performance targets as the Si-based electrodes in Chapter 3. However, a greater emphasis is put on diminishing coulombic inefficiency (CIE) using Li hosts and less emphasis is placed on electrode swelling. The advantages of a carbon host coated in a tin oxide for Li metal electrodes are explored and reported in Sections 5.1 – 5.3 with symmetric, half, and full cell configurations. This work builds on previous research of alkali metal hosts with improved wettability for Li metal electrodes, published in 2017.⁹²

Additional work on novel architectures formed by the carbothermal shock method is then covered in Section 5.4. The challenges associated with this work include (i) controlling the ultrafast synthesis of carbon frameworks by the carbothermal shock method, (ii) obtaining suitable electrolyte for Li metal cycling, and (iii) collaborating with colleagues to confirm the nanostructure of the materials. Two independent architectures are reported using this approach. SEM characterization shows that the unique morphologies are feasible on a small scale by the rapid heating process. More specifically, short timescale of the Joule heating enables the exfoliation of carbon nanofibers and the growth of decorated carbon matrices with transition metal nanoparticles for improved lithium wetting. Future effort will be needed to improve the uniformity of both methods and further validate the cycling performance in lithium metal batteries with modified, nonflammable electrolytes.

Chapter 3: Composites Silicon Electrodes with High Initial Efficiency and Stability

The performance requirements for commercial lithium ion batteries are unlikely to relax. Therefore, the burden lies with battery scientists and researchers to replace conventional materials with high energy density silicon and high nickel content cathodes. In this work, the thickness of the negative electrode is reduced by almost 50% by replacing 30 wt% graphite with unlithiated Si additive. The Si additive is designed to maintain better attachment with the other conductive additives in the negative electrode, bond with binder covalently, and form improved SEI due to surface functionalization. These distinctions are more pronounced in the half cell measurements of the novel negative electrode when compared against the control. Figure 3.1 shows a schematic with magnified microscopy images of the Si additive (left) and a high-capacity NMC particle (right).

The positive electrode consists of 90 wt% 811NMC, a high nickel content cathode without additional modifications or interface engineering. High nickel content cathodes suffer from metal leaching and costly phase transitions, which can form poor interphases during delithiation. Notably, the parent chemistry, LiNiO_2 , is impractically unstable after delithiation even though it offers a high capacity with a high oxidation potential with a more abundant transition metal stoichiometry. In half-cell configurations galvanostatically cycled between 4.2 – 2.4 V, the first cycle delithiation capacity and initial coulombic efficiency (ICE) of the 811 NMC positive electrode are 180 mAh g^{-1} and 86 %, respectively. After cycling at 640 mA g^{-1} for 300 cycles the average CE is 99.77 %, representing a 96 cycle lifetime before reaching 80 % capacity retention.

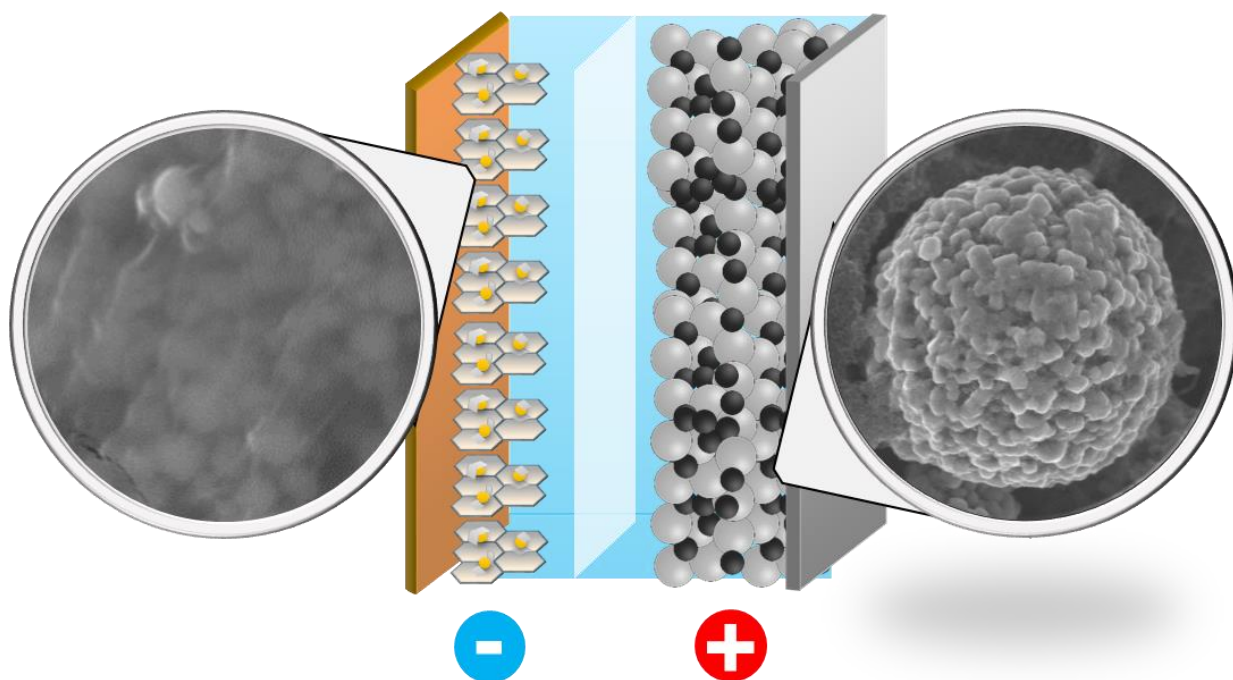


Figure 3.1. (a) Schematic of the energy dense lithium ion battery with a high capacity silicon-based negative electrode and NMC-based positive electrode.

The testing protocol for Si composite electrodes has matured significantly with greater understanding of the lithiation and activation of the electroactive material.^{93–96} The general testing protocol for the half and full cells in this dissertation are given in Table 3.1 after significant review of the literature. The impedance spectra of the lithium ion batteries in these experiments are collected using a Biologic VMP3 multichannel system in a frequency range from 100 kHz to 0.1 Hz. EIS measurements can provide information about transport phenomena in the system, however this information lacks specificity. Ion migration by solid-state diffusion, versus charge transfer through surface films (or interphases) and capacitive processes can be isolated only through equivalent-circuit models. The spectra in this study are best represented by the Randles and Ershler electronic equivalent-circuit model as shown in Figure 3.2. In this circuit, R_s is the ohmic resistance of the electrolyte solution and contacts, C_{dl} is the double-layer capacitance, R_{ct} is the electron

charge transfer resistance, or more specifically the non-rectifying resistance of the cell, and W is the Warburg impedance. When SEI layers form on the electroactive materials, the impedance spectra changes and the model takes on additional components for each layer, R_{SEI} and C_{SEI} , respectively, in Figure 3.2 (b). The layers within conventional SEI can also be distinguished by separate semi-circles.

Table 3.1. Testing protocol for EIS, CCCV, voltage drop, LSV, and impedance tests.

Cell Design	Test	Cell Comp.	Protocol
2032 coin cells 0.87 cm ² area separator: 2400 Celgard	EIS	532NMC 30Si58Gr	1 MHz – 100 mHz after assembly + wetting
	CCCV	532NMC 30Si58Gr	Hold at 1.5 V _{tap} for 24 hours CC: 4.3 – 3.0 V CV: 4.3V hold for 5 min. until 60 mA g ⁻¹ 1 formation cycle: 60 mA g ⁻¹ ch/dis 5 cycles: 150 mA g ⁻¹ ch/dis, then 300 mA g ⁻¹ ch/dis
	Voltage Drop	532NMC 30Si58Gr	CC: 4.3 – 3.0 V 1 formation cycle: 60 mA g ⁻¹ ch/dis CCCV: Charge to 4.3 V and hold 24 hours Measure voltage drop every 120 hours
	LSV	Li on Cu Al-coated SS	0.1 mV sec ⁻¹ from 0.5 – 6.5 V
	Impedance Test	532NMC 30Si58Gr	Same as the CCV test except after each charge step, perform EIS.

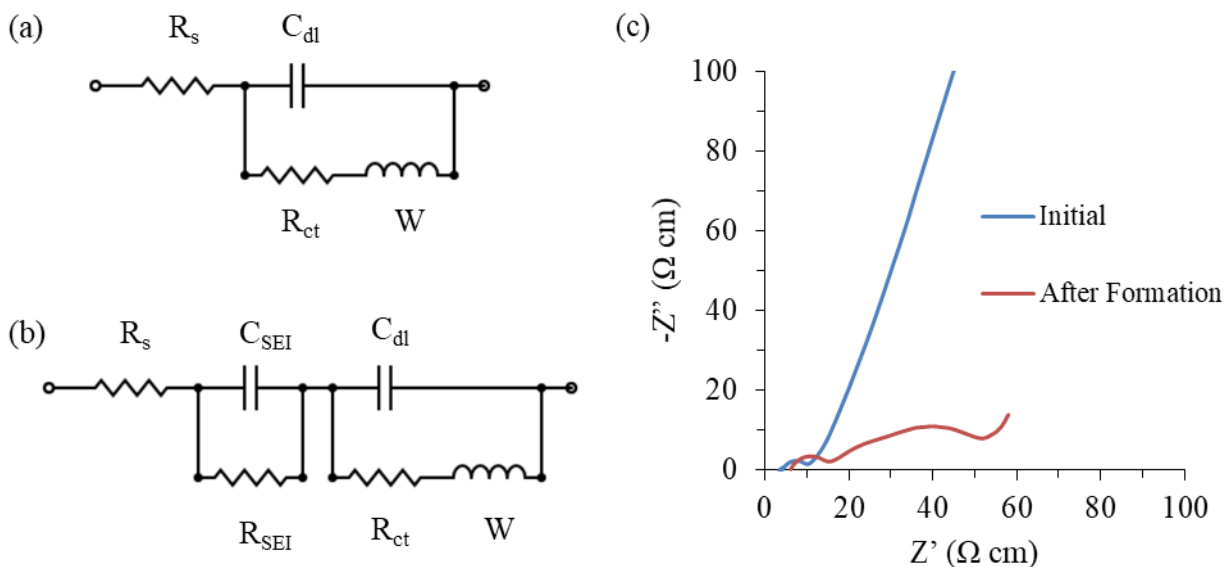


Figure 3.2. Randles and Ershler electronic equivalent-circuit model for lithium ion batteries (a) before SEI is formed and (b) after. (c) Impedance spectra of the NMC532||Si composite full cells with LiPAA binder before and after SEI formation.

3.1. A Solution-based Approach to Amine-functionalized Silicon Nanoparticles

This section outlines the preparation of functionalized and coated silicon nanoparticles for high energy density lithium ion batteries. A provisional patent was submitted to protect and encompass the innovations from this research. The synthesis omits all high temperature annealing steps and chemical etching processing. The silicon particles are functionalized with amine groups in solution, and concurrently, graphene oxide is partially chemically reduced in a dilute acid. The functionalized silicon particles are dropwise added to the dispersion of suspended, partially reduced graphene and fall out of the ethanol-based solution. After the reaction is given sufficient time to equilibrate, the particles can be cleaned and collected for battery applications. In one proposed application, the invention is the sole electroactive material in negative electrodes for

LIBs. In another, the invention is mixed with other electroactive materials for a dense composite negative electrode for LIBs. Details of the synthesis are as follows:

1. Surface functionalization of silicon nanoparticles. Disperse silicon nanoparticles (50 nm average diameter) in ethanol and bath ultrasonicate for 1 hour. Transfer the mixture to a stir plate and mix at 1000 rpm. Slowly add the functionalizing additive and stir.

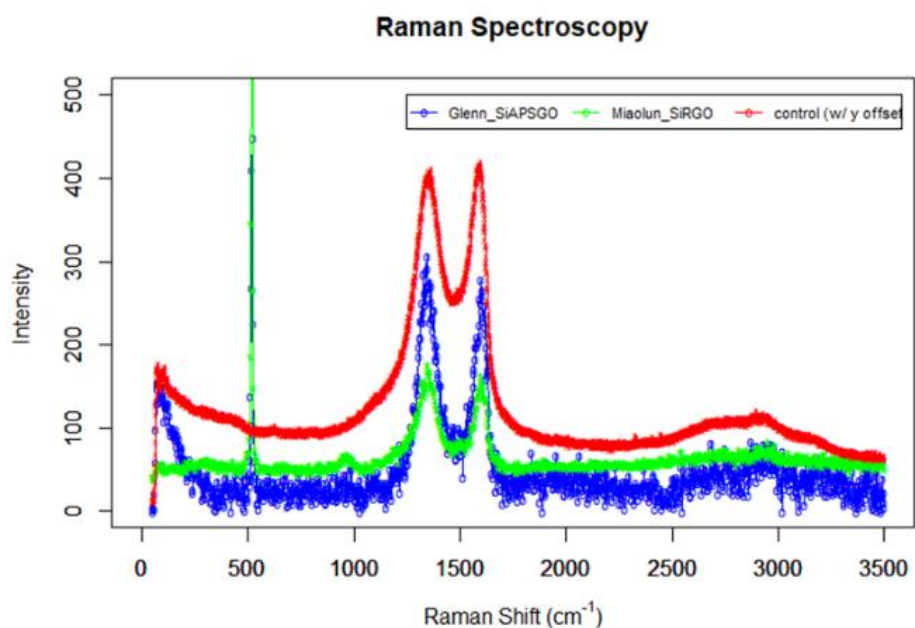


Figure 3.1.1. (a) Raman spectra of the partially reduced graphene oxide (red) versus two control samples of graphene oxide reduced at 800 °C in argon.

2. Chemical reduction of graphene oxide. Dilute commercial single-layer graphene oxide in an additional aqueous solution and stir. Add an acid and let reduce. Dilute the dispersion of partially reduced graphene oxide (pRGO) into a large reservoir of distilled water.

3. Functionalizing Si on pRGO. Soon after diluting the pRGO dispersion, check the pH of the solution and stir. Collect and add Si:pRGO by weight (between 10:1 and 0.5:1 window of interest). Let the reaction progress in the acidic solution while stirring, then let sit. Collect the

reacted particulates from the bottom of the suspension to centrifuge. Wash in ethanol/water at least 3 times, removing the top, unreacted and fine particulate GO and Si. Freeze dry the material to weigh, characterize, and mix for battery electrodes. Subsequent annealing can ensure further reduction of the graphene oxide coating however it is not required for stable electrochemical performance.

Novel battery grade electrodes are synthesized in the lab while control electrodes were graciously provided by Argonne's Cell Analysis, Modeling, and Prototyping (CAMP) facility. The functionalized Si additive does not succumb to catalytic reaction in the presence of carbon and aqueous solution during slurry preparation as seen in Figure 3.1.2. (e) - (g). The reaction of the silicon surface, without prior functionalization or oxidation, in the presence of water and carbon, is particularly critical to the performance of the electroactive materials.⁹⁷ Examples of unprotected and reactive Si additives in aqueous composite slurries have been reported and identified in the literature.^{98,99} Throughout these experiments, the Si additive has been observed to outgas and reduce in aqueous solution while mixing in the presence of carbon black. Figures 3.1.2. (a) - (d) show that after mixing in a ThinkyMixer for 15 minutes with four ceramic zirconia balls at 1500 rpm, the poorly functionalized Si additive, outgasses and turns black. Upon further testing, all of the electroactive Si additive has been reduced to colorless SiO_x , thereby leaving the slurry black from the remaining graphite and carbon black. When the additive is well functionalized and mixed under more moderate conditions, (1200rpm for 4 minute increments) the slurry is uniform without any outgassing reactions, as seen in Figures 3.1.2 (e) – (g). Given that the Si nanoparticles have not been treated by a mild oxidation process, this is a novel solution to protect Si during the slurry preparation process.

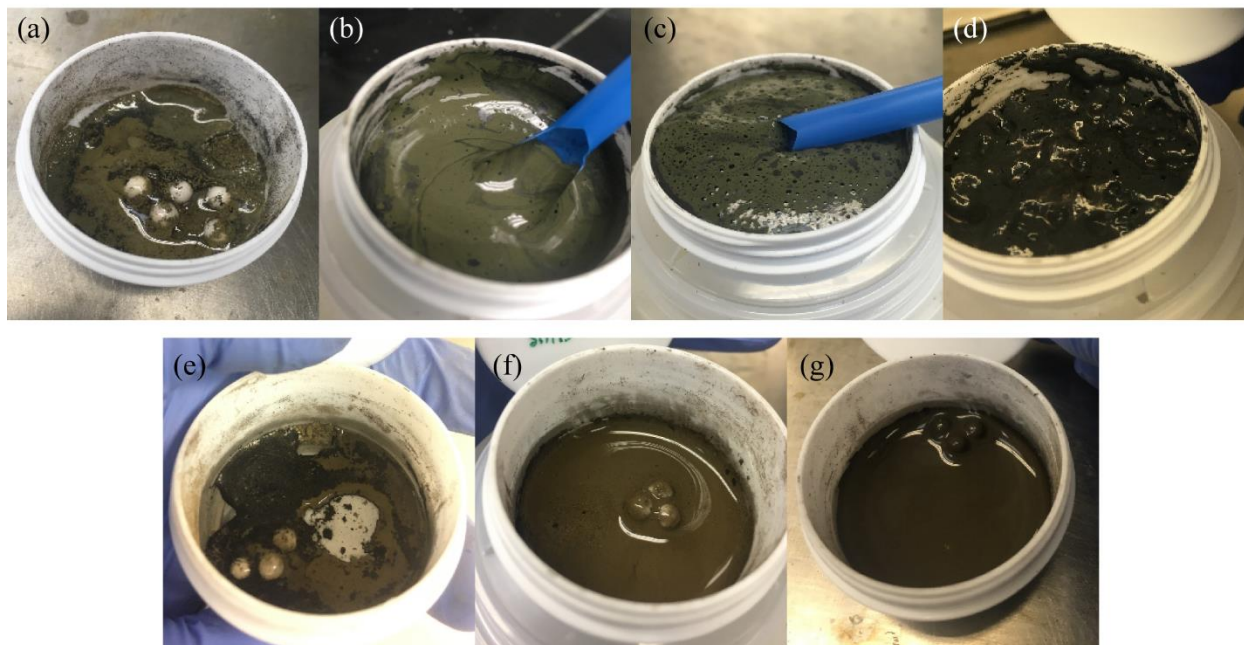


Figure 3.1.2. Comparison of slurry preparation which succumbs to (a-d) and avoids (e-g) catalytic reaction of the Si additive. Additive, which is not properly functionalized and prepared, can react exothermically in aqueous solution with carbon to release gas.

Cathode and anode powders were sourced from MTI, ACS Materials, and Sigma Aldrich. Oxygen-sensitive materials such as the Si nanopowder, 811NMC electrodes, etc. are stored in an argon filled glovebox with $O_2 < 0.01$ ppm and $H_2O < 0.01$ ppm. Initial screening of electroactive materials includes cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic cycling tests in half cell configurations. After the initial electrochemical screening tests, crude materials were investigated by x-ray diffraction, scanning electron microscopy, as well as Raman and Fourier transform infrared spectroscopy (FTIR).

Throughout the preliminary work, various cathode materials have been used based on availability, project focus, and energy density requirements. Initially, the full cell configuration incorporated NMC811 positive electrodes due to their high theoretical energy density and anticipated reduction in cost. However, as will be further discussed in section 4.1, the interfacial

stability of NMC811 is low without further surface modifications or tailored electrolyte. During delithiation beyond 80 – 90 % state of charge, the structure of NMC811 collapses such that transition metal ions (Ni and Mn, specifically) diffuse out and radical oxygen species react with the electrolyte to form thick SEI layers. Additional optimization of a tailored electrolyte and positive electrode to balance against the high capacity Si composite are described in the subsequent chapters.

3.2. Morphology and Dispersion of Si Additive

The morphology and dispersion of the Si additive in the composite negative electrode is shown in Figure 3.2.1. Figure 3.2.1 (a) shows a typical graphite particle, uniformly coated by the silicon additive. Small portions of the graphite particle remain uncovered as determined by the corresponding EDS images in Figure 3.2.1 (c) – (e). Under closer examination, RGO is identified, wrapping the silicon particles. As a result, the presence of oxygen on the graphite particle can be attributed to RGO and binder (Figure 3.2.1 (e)). A zoomed out backscattering image of the negative electrode reveals the roughly random dispersion of Si additive throughout the composite electrode. In comparison to composite electrodes without functionalized Si additive, this electrode shows less clusters of aggregated silicon nanoparticles and less outgassing reactions during slurry preparation. Under acidic conditions, the amine-functionalized silicon surface favorably attaches to carboxyl groups on the RGO and binder. The RGO and binder are thoroughly mixed in the composite electrode such that the functionalized additive disperses as a thin layer on the graphite particles. The thorough mixing of the electrode components and the Si additive is further confirmed in the corresponding EDS images from Figure 3.2.1 (f) – (h).

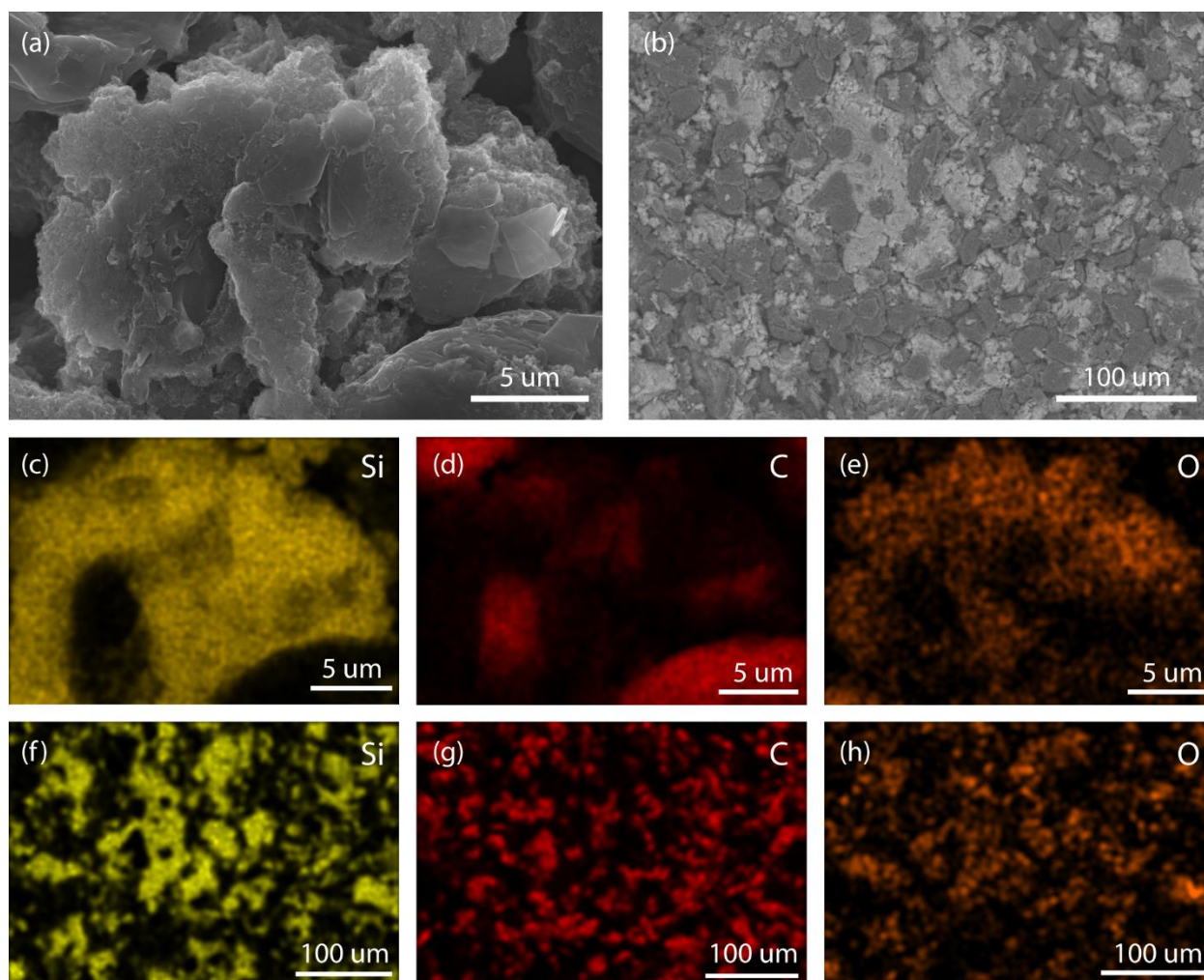


Figure 3.2.1. Morphology and structure of the functionalized silicon electrode. (a) SEM images of a graphite particle coated with the functionalized silicon additive. (b) Backscattered SEM image of the composite silicon electrode with silicon additive interspersed throughout the composition. (c-e) EDS images of the single graphite particle with silicon additive uniformly attached to the edge and basal planes. (f-h) EDS images of the composite silicon electrode with uniform mixing of graphite particle with and without the functionalized silicon additive.

The dispersion of Si additive on large graphite particles is further confirmed by the SEM and EDS images in Figure 3.2.2. Figure 3.2.2 (a) and (b) show a cluster of large graphite particles isolated from the Si composite slurry on a Cu substrate (a) with and (b) without EDS overlaid on

the region of interest (ROI), respectively. The inset of (b) plots the corresponding spectra and shows the strong presence of Si (red), O (blue), and C (green) on the graphite cluster. By looking at the x-rays emitted around 1.739 keV, it can be concluded that there is a strong signal for Si in the ROI. The same can also be said of C (0.277) and O (0.525), which are present in the sample from the graphite and GO. It is interesting to note that the silicon additive coats the graphite particles and reduces the C signal on parts of the cluster. This is in strong contrast to pure mixing of Si nanoparticles with graphite. In previous work, these materials suffer phase separation with significant implications for cycling performance.¹⁰⁰ By using a vacuum deposition method on the graphite particles, a more uniform coating could be achieved. However, the Si additive is attached and wrapped by pRGO sheets which were synthesized by the solution-based process. Therefore, even though the dispersion of the Si additive is not ideal, it is far superior to clustered Si nanoparticles which are crudely mixed into the graphite-dominant slurry.

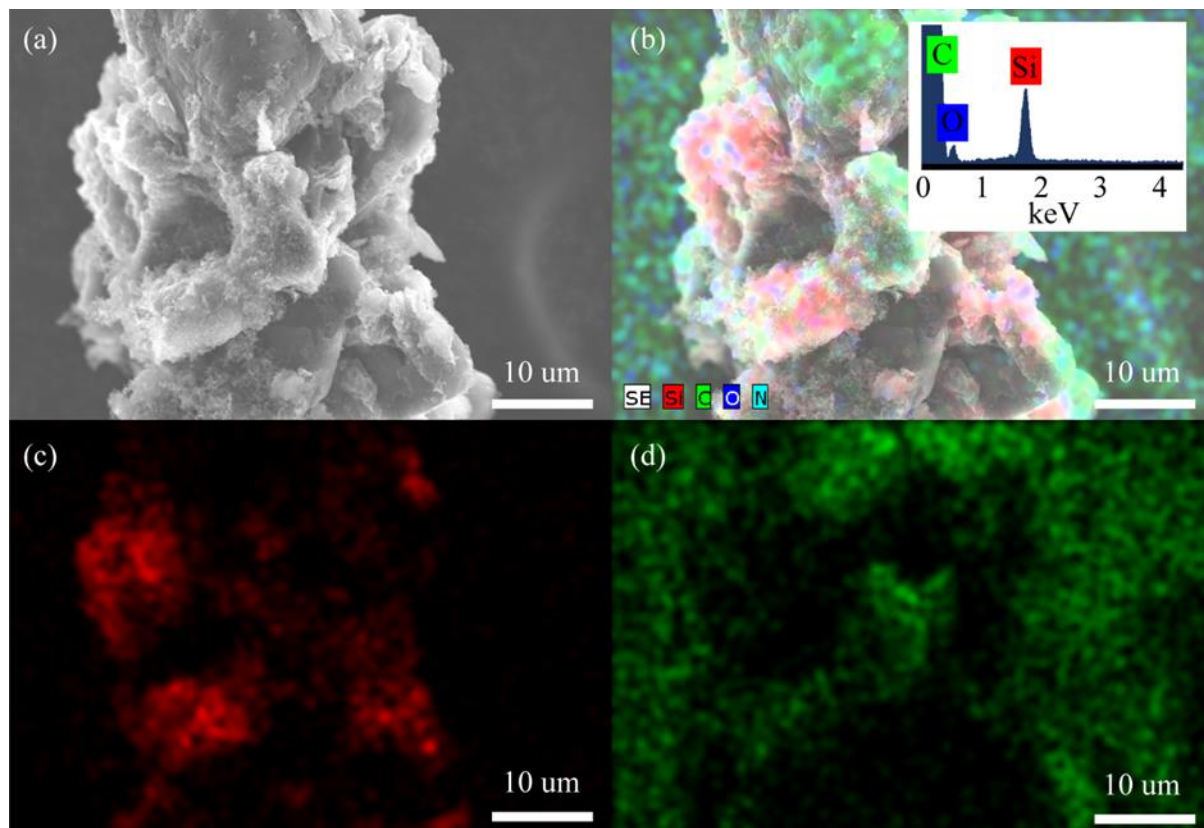


Figure 3.2.2. Morphology and dispersion of the functionalized silicon additive on graphite particles isolated from the slurry. (a) SEM image of a cluster of graphite particles. (b) EDS image with the spectra for Si (red), C (green), O (dark blue), and N (light blue) on top of the same ROI. Inset is the spectra count with peaks labeled for Si, C, and O. (c-d) EDS images of the same ROI with only Si and C counts included, respectively.

3.3. Composite Silicon Electrochemical Performance

Half-cell configurations of the Si composite negative electrode outperform composite electrodes with similar Si content. Figure 3.3.1 shows the rate performance, long term retention, electrochemical impedance spectra, initial coulombic efficiency (ICE), extended coulombic efficiency (CE), and cyclic voltammogram of the reported and control Si composite electrodes. In comparison to the novel negative electrode, the control contains 30 wt% Si nanoparticles mixed with graphite without further functionalization or protection. The control electrode includes the same weight percentage of additive but a higher overall weight ratio of crude Si material. The impedance spectra of multiple unlithiated electrodes with the drop-in additive were tested to investigate the impact of the additive on the charge transfer and diffusion resistance. The plot in Figure 3.3.1 (c) shows that low charge transfer resistance less than $20 \Omega \text{ cm}^{-2}$ is largely consistent across the batch with correspondingly low Warburg diffusion resistance. Variations between the impedance spectra in the batch are complicated by impurities and inconsistencies from the Li metal counter/reference electrode. Due to the functionalization of the silicon surface, it is unsurprising that the Si composite electrode shows higher charge transfer resistance than the control sample (Figure 3.3.1 (c)). Further work can also be done to optimize the slurry coating and electrode calendaring process. The electrode reported in Figure 3.2.1 has a mass loading of 1.88 mg cm^{-2} and an electrode density of 0.67 g cm^{-3} .

The most apparent improvement in performance comes from the increased efficiency of the functionalized Si additive during the first 5 cycles without prelithiation additives or procedures (Figure 3.3.1 (d)). The ICE of the negative electrodes improves from 90 to 92 %, and in subsequent cycles, the efficiency of the functionalized negative electrode jumps up to 99 %, as seen in Figure 3.3.1 (e). Both electrodes are slowly activated under the same conditions to mimic the formation cycles of full pouch cells. The improvements to the SEI formation and nanostructure of the Si additive are further confirmed by the delithiation capacity and CE of the negative electrode during extended cycling in Figures 3.3.1 (b) and (e). The functionalized electrode offers 1350 mAh g⁻¹ capacity at 80 mA g⁻¹ versus 1100 mAh g⁻¹ for the control electrode at the same current density. The functionalized negative electrode also quickly exceeds 99.5 % CE at 320 mA g⁻¹ after undergoing preliminary rate cycling up to 640 mA g⁻¹ in the first 16 cycles. At a current density of 320 mA g⁻¹, the functionalized electrode has 0.1815 % average irreversible capacity loss per cycle and 99.67% average CE. Even though the CE after activation remains insufficient for most commercial applications, this is a significant improvement over the control electrode which fails to reach 99.5% CE at 320 mA g⁻¹ before failure. Further characterization of the rate performance up to 640 mA g⁻¹ is displayed in Figure 3.3.1 (a). After cycling at 320 mA g⁻¹, the functionalized negative electrode retains over 80 % of its initial capacity (normalized by the first discharge capacity at 320 mA g⁻¹).

Reducing the voltage window and optimizing the electrolyte further complicates the benchmarks of a high energy density negative electrode. The negative electrodes in half-cell configurations are tested with a wide voltage window (0.005 – 1.0 V) without prelithiation agents or specialty additives. In Figure 3.3.1 (f), cyclic voltammetry of the negative electrode further confirms the phase transition from amorphous into crystalline Li₁₅Si₄ below 70 mV as reported by

Obrovac et al.²² There are many issues associated with the c-Si which summarily lead to high internal stress and irreversibility. Therefore, the improvement in the activation efficiency can be viewed more favorably given the excessive stress encumbered by the applied voltage window. Previous work using three electrode configurations reveals that the negative electrode need not be cycled through the full voltage window.^{20,89,97} Further analysis has emphasized the importance of tailoring the voltage window given the reversibility of the composite electrodes in various electrolytes. Future work will seek to quell irreversible capacity loss by improving the electrode durability and electrolyte stability for Si-based cycling.

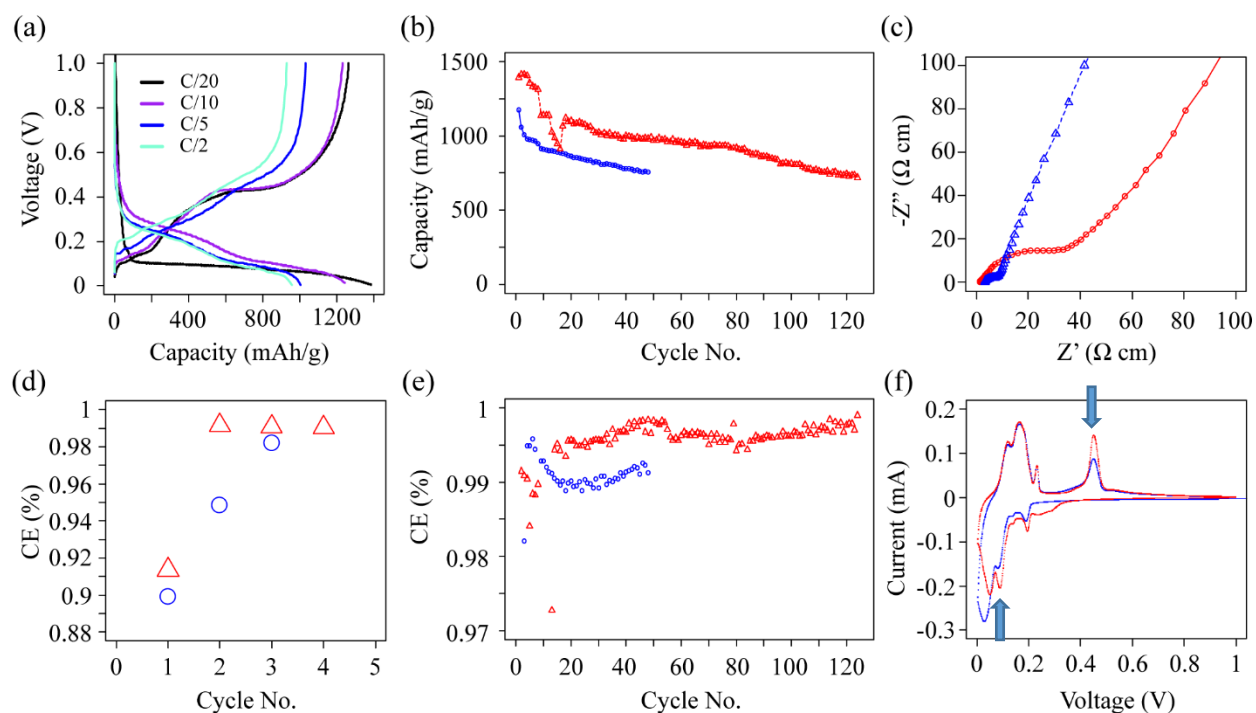


Figure 3.3.1. Electrochemical performance of the Composite Si (red) and control electrode (blue) in half cell configurations. (a) Rate performance of the Si composite electrode at 80 (black), 160 (purple), 320 (blue), and 640 mA g⁻¹ (aqua). (b) The delithiation capacity of the control and functionalized Si composite electrodes. Although the functionalized composite electrode contains less Si by weight, it boasts a higher delithiation capacity. (c) The impedance spectra of the control

and functionalized Si composite electrodes before cycling. (d) The initial activation efficiency of the functionalized and control electrodes. The functionalized electrode boasts 92 % ICE and over 99 % CE after the first cycle. (e) The CE of the electrodes after 4 cycles at 80 mA g⁻¹, 4 cycles at 160 mA g⁻¹, 4 cycles at 320 mA g⁻¹, 4 cycles at 640 mA g⁻¹, and the preceding cycles all at 160 mA g⁻¹. (f) Cyclic voltammogram with the first and second cycles of the functionalized negative electrode between 5 mV and 1 V at 0.02 mV s⁻¹. The blue arrows indicate phase transitions between amorphous Li_xSi and crystalline Li₁₅Si₄.

To better understand the advantages of the composite silicon electrode design, silicon electrodes with Si nanoparticles (nano-Si) as the only electroactive material are synthesized and tested without further modification. The nano-Si electrode slurries consist of 60 wt% of 30 to 50 nm Si nanoparticles, 20 wt% carbon black additive, and 20 wt% of sodium alginate in approximately 10 wt% aqueous slurry. The slurries are cast by a four-sided film applicator and achieve 0.33 mg/cm² active mass loading. Electrodes with a 1.25 cm diameter are punched out for testing in coin cells against Li metal between 0.005 – 1V. The cells are activated at C/20 for four cycles and then cycled at 1C, equivalent to approximately 3590 mA g⁻¹, for 1000 cycles.

The results from EIS and galvanostatic cycling of the nano-Si electrode is given in Figure 3.3.2. The half-cell is tested with 1.0 M LiPF₆ in EC:DEC (50:50 w%) with 10 wt% FEC. Figure 3.3.2 (a) shows the cycling profiles of the electrode. The ICE of the electrode is unknown due to disruptions to the cell but the 2nd through 4th cycle CEs are 99.8, 98.8, and 98.8 %, respectively. This is only slightly lower than the activation CE of the composite based electrode. This performance can be attributed to the efficacy of the FEC-derived SEI on the low mass loading electrode (0.55 mg cm⁻² total mass loading). The high surface area Si nanoparticle are well attached by the sodium alginate binder to the current collector and the conductive carbon black. The

impedance spectra in Figure 3.3.2 (b) further confirms the relatively low high charge transfer resistance of the nano-Si electrode without a stable conductive matrix. In the composite Si electrode, graphite serves as a stable conductive matrix to attach to the Si additive and reduce the total volume expansion of the electrode, thereby improving the integrity of the electrode.

The extended cycling performance of the nano-Si electrode is presented in Figure 3.3.2 (c) with the delithiation capacity (mAh g^{-1}), the coulombic efficiency (%), and the capacity retained per cycle (%). The performance of the nano-Si electrode indicates it will perform worse in a full cell than the functionalized Si composite even though it eventually has a higher CE and a higher initial lithiation capacity. In particular, the capacity retained per cycle by the nano-Si electrode is only 99.01 % after 1000 cycles compared to 99.82 % after 120 cycles with the functionalized Si composite. The capacity retained per cycle indicates the reversibility of the delithiation capacity from the previous cycle to the current cycle ($Q_{n,\text{de}}/Q_{n-1,\text{de}}$). This is not the same as the CE ($Q_{n,\text{dis}}/Q_{n,\text{ch}}$) of the cell and provides a separate metric for the degradation and performance of electrochemical cells.¹⁰¹ Past work emphasized the importance of time (i.e. aging) as the primary factor leading to coulombic inefficiency in stable full cells with low-strain electrodes.¹⁰² However, silicon electrodes undergo a more demanding alloying reaction than conventional electroactive materials which further complicates the relationship between observables during galvanostatic cycling and causality. In particular, coulombic inefficiency (CIE) and capacity retained can be superficially related to additional SEI formation and active material loss, respectively, in Si-based half-cells.

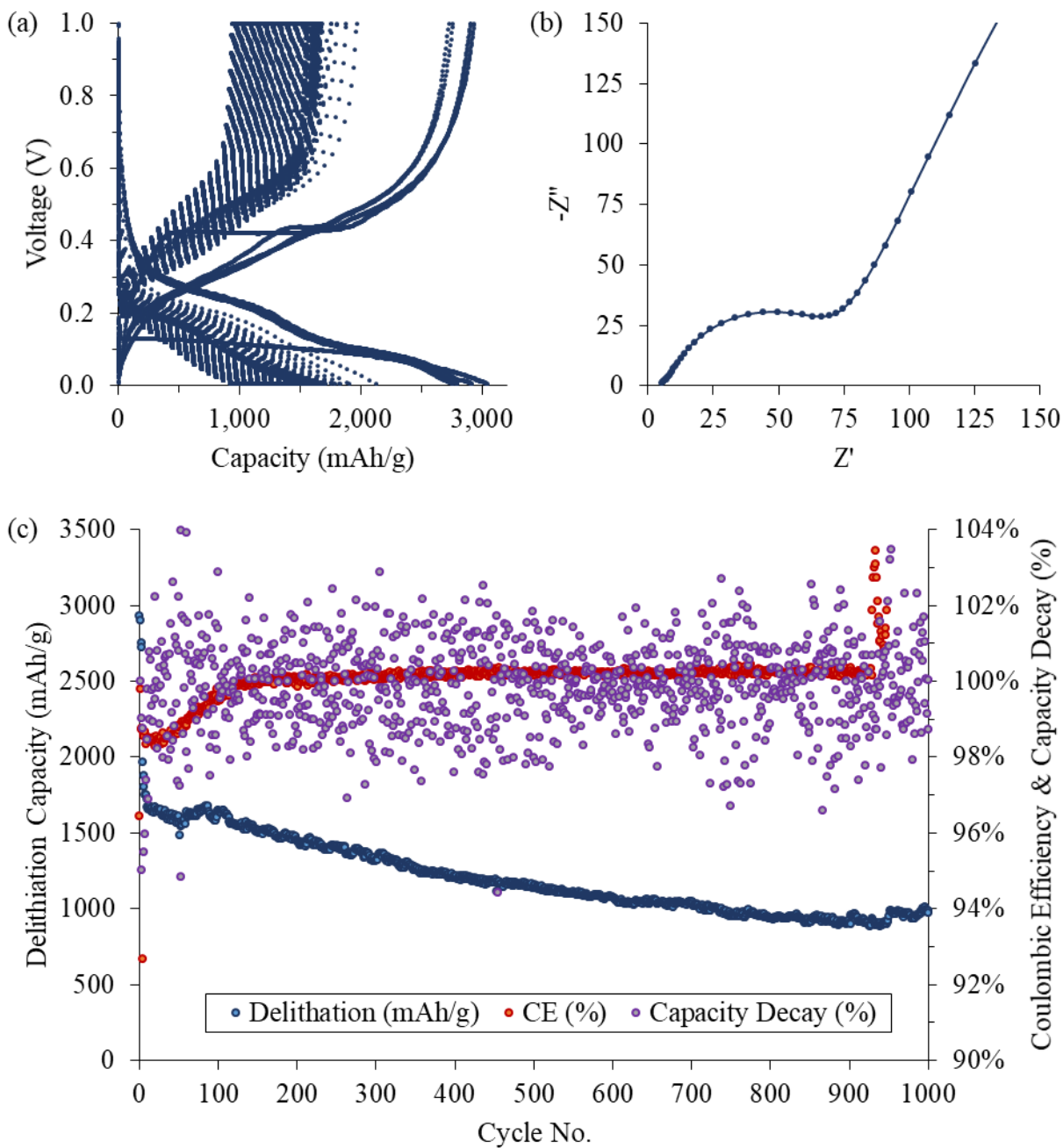


Figure 3.3.2. (a) Capacity vs. voltage of the nano-Si electrode in a half cell configuration and 1.0 M LiPF_6 EC:DEC (50:50 wt%) + 10 wt% FEC electrolyte. (b) Impedance spectra of the nano-Si electrode before cycling. (c) Plot of the delithiation capacity, CE, and capacity retained of the nano-Si||Li cell between 0.005 – 1 V at C/20 for the first four cycles followed by 1C rate for 1000 cycles.

The extended cycling performance of the nano-Si electrode below is a good example of the importance and mutual exclusivity of both CE and capacity retained for electrochemical characterization. The nano-Si electrode is cycled at 1C between 0.005 to 1 V, using constant current (CC) protocol. The electrode starts out with 98.44 % average CE and 99.01 % average capacity retained in the first 50 cycles at 1C. However, the CE rises to above unity ($> 100\%$) after 125 cycles and the average CE rises to 100.04 % and 100.65 % after 930 cycles and 1000 cycles, respectively. In comparison, while the capacity retained varies more significantly from cycle to cycle, after 930 cycles the average capacity retained is 99.89 % and, similarly, after another 70 cycles it rises by 0.02 % to 99.91 %. This discrepancy in the CE can be explained by two likely phenomena.

The first phenomena was proposed by Gyenes *et al.* from a study on LCO||Gr cells.¹⁰³ Full cells with consecutive CEs greater than unity are interpreted and analyzed by the lithiated “overhang” of the negative graphite electrode. In these cells, storage at a low or high state-of-charge (SOC) results in less or more diffusion of lithium into the outer overhanging negative electrode, respectively. However, in a half cell, the area of the Li counter electrode exceeds that of the active electrode and complicates a description related to the overhang phenomena. Instead, it is speculated that the greater than unity CE is the result of degradation of the Li counter electrode. As the surface of the Li counter electrode directly opposite the nano-Si electrode cracks and develops dead-Li, fresh Li is stripped at a lower overpotential from the overhanging parts of the counter electrode. This is one explanation for the greater than unity CE of the nano-Si electrode.

The other most likely culprit for the observed phenomena is some form of ohmic, concentration-driven, or electrochemical polarization in the electrode. For instance, trace polarizable species that do not lithiate the nano-Si electrode but migrate and adsorb or react with

the Li counter electrode. The polarizable impurities must be unable to react or lithiate the nano-Si electrode since the electrode regained no trapped capacity in subsequent cycles. The source of the polarization is further obscured by the conditions on the electrode after cycling for over 100 hours.

Whatever is causing the anomalous CE, the result is the obfuscation of the nano-Si CE. As a result, even though the capacity retained of the electrode fluctuates widely with a standard deviation of 1.47% and lacks precision. This metric is accurate across the cycling of the electrode and can be more simply attributed to active material loss (due to detachment or delamination) or excessive SEI formation. Previous works by Wetjen *et al.* indicated that Si nanoparticles in a composite electrode undergo permanent volume expansion by approximately 700 % after 60 cycles related to the repeated insertion and extraction of Li. This results in a nanoporous Si network with lower internal stresses during cycling but also higher surface area that is still vulnerable to perpetual SEI formation while cycling. It is also important to note that the degree of volume and surface area expansion of a sphere do follow a one-to-one ratio. In the context of a Si nanoparticle, the surface area increases by ~244 % when the volume increases by 380 % during lithiation from Si to $\text{Li}_{3.34}\text{Si}$ (i.e. $\text{Li}_{15}\text{Si}_4$). However, this changes when the Si nanoparticles degrade into individual nanoporous networks. It is reasonable to assume that at some point, the nanoporous network reaches a final state such that there are less new surfaces for continual SEI growth.¹⁰⁴ This passivation is then supplanted by the loss of active material. This is further justified by the difference in impedance and coulombic inefficiency between the functionalized and non-functionalized Si composite cells. It is also supported by post-mortem analysis and reserve engineering from full cells with a limited reservoir of Li. For instance, as will be further explained in Section 3.5, full cells with the functionalized Si composite electrode eventually show degradation phenomena associated with active material loss which leads to sudden failure of the

full cell which cannot be resolved by adding new electrolyte to the system. As a result, the capacity retained per cycle of Si-based electrodes is an important metric to use in conjunction with CE. By extension, the composite silicon electrode described in Section 3.1 and 3.2 performs well in half cell configurations.

3.4. High-mass loading electrodes

High mass loading and binder-less electrodes are appealing for commercial applications that prioritize energy dense cells with minimal inactive material. However, these two attributes are challenging to achieve in the same electrode design. High mass loading materials often suffer from slow diffusion and charge transfer which is best mitigated by improving the electrode tortuosity, changing the electrolyte system, or increasing the inactive binder and conductive additive components. Binder-less systems often suffer from delamination challenges from the current collector and active material loss which can lead to a perpetually higher applied current density and higher cell overpotentials.

In this study, the solution-based approach for functionalized Si composite electrodes is applied to high mass loading and binder-less electrodes. SEM images of the Si additive and the pressed electrode are given in Figure 3.4.1. (a) and (b), respectively. The Si additive is processed by the same solution-based method described in Section 3.1. In the SEM image, the partially reduced graphene oxide (pRGO) is visible wrapping the silicon nanoparticles. The particles attached to the sheets due to the electrostatic interactions between the negatively charge GO defects and the amine-functionalized Si nanoparticles, respectively. An electrode with 5 wt% LiPAA and a binder-less electrode are both fabricated using the same batch of Si additive. However, the mass loading of the electrode with binder was $> 5 \text{ mg/cm}^2$ and the performance did not warrant further analysis. The composition of the binder-less electrode is 23.75 wt% Si

additive, 71.25 wt% Gr, and 5 wt% CB. As seen in Section 3.2, the Si additive mixes well with the graphite matrix and spreads across the binder-less electrode rather than clumping in large clusters. The total mass loading of the binder-less electrode is 4.84 mg/cm^2 and the thickness is approximately $95 \text{ }\mu\text{m}$ which corresponds to an electrode density of approximately 0.51 mg cm^{-3} .

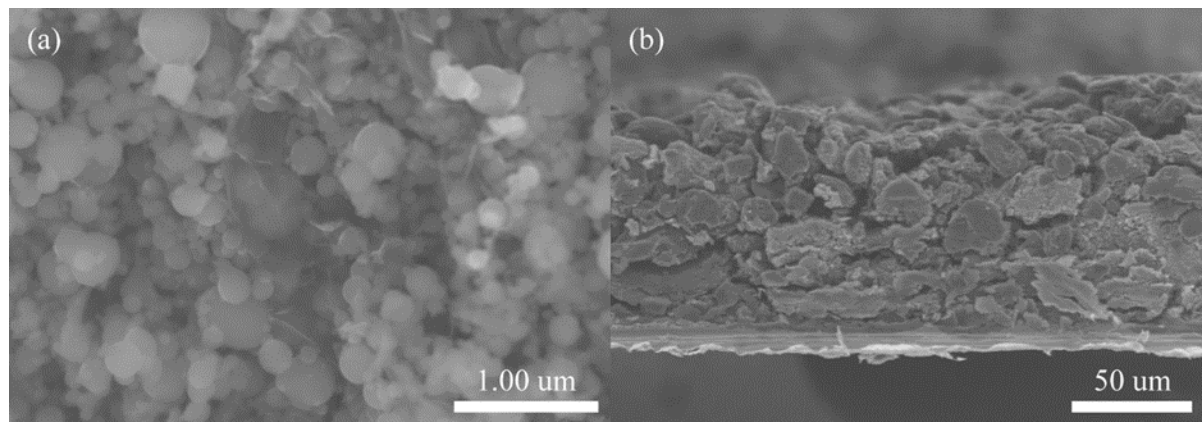


Figure 3.4.1. (a) SEM image of the Si additive with graphene sheets wrapped on the Si nanoparticles. The solution-based process for the additive is consistent with Section 3.1. (b) The high mass loading electrode is just under $100 \text{ }\mu\text{m}$ thick with 14 mg cm^{-2} mass loading.

The theoretical capacity of the binder-less electrode, given that the Si additive contains approximately 20 wt% carbon, is 945 mAh g^{-1} . The electrode delivers 925 mAh g^{-1} or 81% of its theoretical capacity from the first lithiation process with an ICE of 86.0%. The electrode is cycled for an additional 4 cycles at C/20 before cycling at C/5. Figure 3.4.2 shows the delithiation capacity (mAh g^{-1}), CE (%), and retained capacity per cycle (%) of the binder-less and high mass loading electrode. The average CE and retained capacity per cycle of the electrode after the first 30 cycles at C/5 is 98.91 % and 99.07 %, respectively. However, these values rise to 99.59 % and 99.65 % after 152 cycles. This is comparable to the 0.1815 % average irreversible capacity loss per cycle and 99.67 % average CE of the low mass loading electrode from Section 3.3, although the weight ratio of Si additive is 6.25 % lower and the electrode

thickness is almost 4 times higher. In this work, a high mass loading Si composite electrode is demonstrated with high capacity retention per cycle at close to the theoretical capacity.

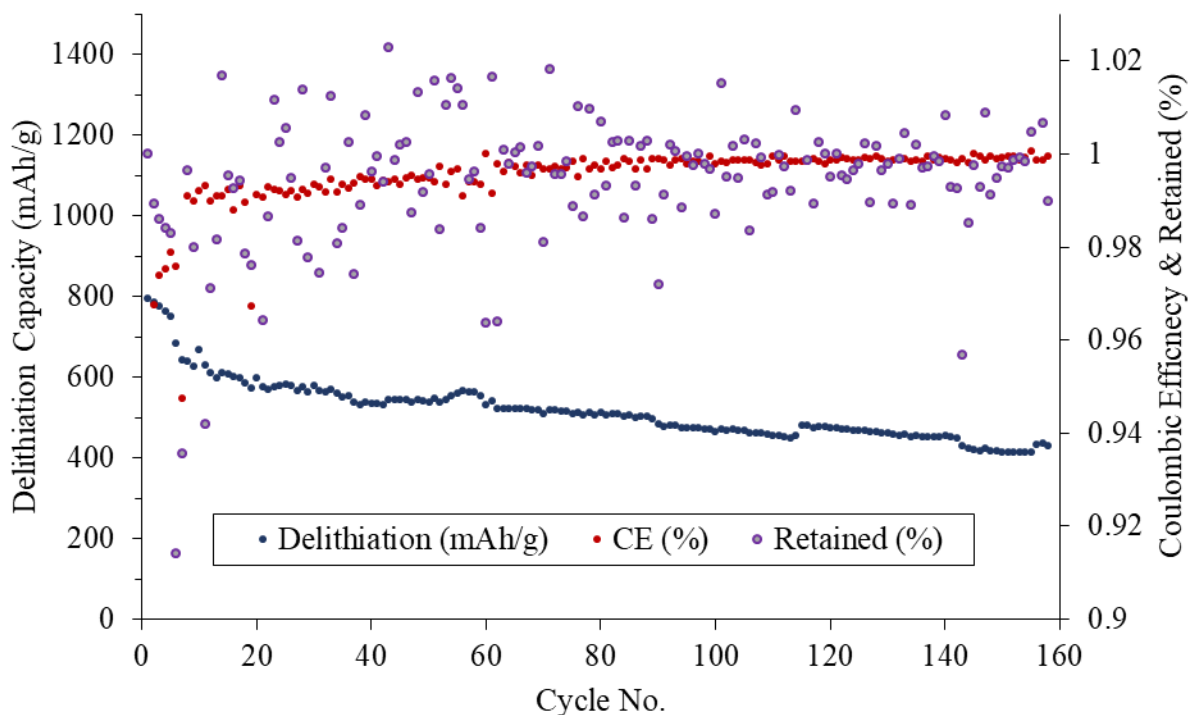


Figure 3.4.2. Electrochemical performance of the high-mass loading and binder-less Si composite electrodes in a half cell configuration.

A separate study published in *Advanced Energy Materials* described the design and performance of a conductive nanofiber network for thick and energy dense phosphate-based positive electrodes. In Figure 3.4.3, the robust electrical networks consisting of negatively charged cellulose nanofibers and carbon black is depicted relative to a conventional LFP electrode with carbon black arbitrarily dispersed throughout the electrode. Additional measurements reveal a shorter ion transport path in the high mass loading, 60 m/cm², lithium iron phosphate (LFP) electrodes. The electrode retained 91% of its capacity after cycling at 2 mA

cm⁻² for 150 cycles. The novel electrode architecture significantly increased the functional mass-loading of a reliable cathode material, thereby increasing the energy density.

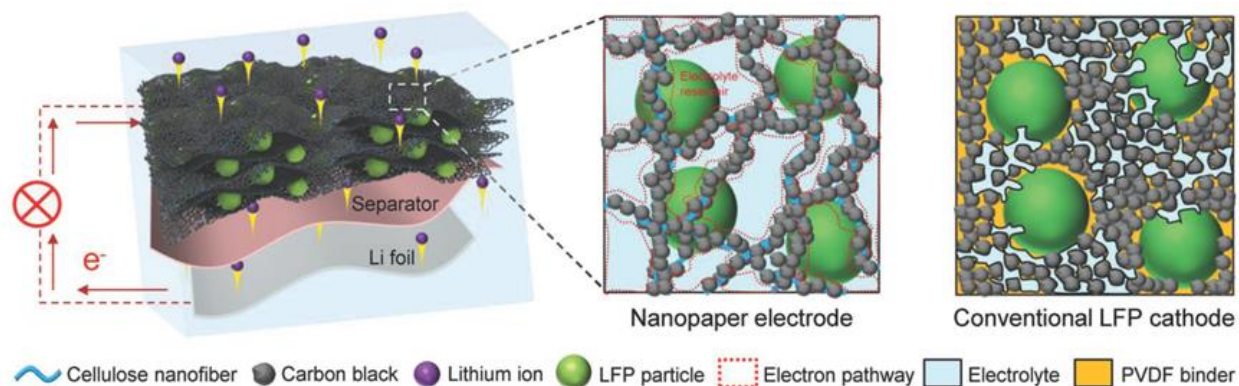


Figure 3.4.3. Schematic illustrating the ion/electron conductive pathways in the nano-paper electrode and spatial arrangement of the electrode materials in comparison to a conventional LFP cathode.

3.5. Analysis of the Voltage Window for Silicon-based Full Cells

Thorough experiments were performed to investigate the ideal voltage window for balancing the retention and energy density of Composite Si||NMC full cells. Given the finite amount of Li in full cell configurations, this work shows that avoiding the phase transition of silicon at 3.25 V in cell configurations with NMC532 greatly improves retention, albeit while sacrificing the volumetric energy density by 15 - 30 %. Figure 3.3.2a shows the capacity versus voltage of NMC532||Si Composite full cells cycled with 3.0 and 3.25 V lower cutoff voltages (LCV). Future work will seek to improve the capacity retention and rate performance of the drop-in Si additive while maintaining or improving the activation CE and initial capacity. Although the 3.0 LCV supports almost 700 Wh L⁻¹ energy density (Figure 3.3.2 c), the retention drop below 80 % within 20 cycles (Figure 3.3.2 d). In comparison, the 3.25 LCV cell starts at about 600 Wh L⁻¹ but maintains over 85 % of its capacity after 50 cycles. This corresponds to a 0.75 % average

irreversible capacity loss by the 3.0 LCV cell compared to 0.31 % irreversible capacity loss by the 3.25 LCV cell. Future work can investigate optimizing the exact LCV further to balance retention and energy density.

By increasing the ratio of active silicon, reducing the electrode thickness, and avoiding the crystalline to amorphous phase transition below 3.25 V, full cells could be optimized for improved energy density with sufficient retention. The exact cell potential of the phase transition is determined by $dQ\ dV^{-1}$ analysis through the full voltage window of 4.35 to 3.0 V (Figure 3.3.2b). The slight variation of the cell potential between batches with different mass loadings and areal capacities suggests that the phase transition is likely dependent on state-of-charge (SOC) rather than cell potential. Experiments to optimize the upper cutoff voltage (UCV) also provided unique feedback. Full cell NMC532||Si Composite configurations charged up to 4.35 V show better retention than cells charged to 4.0 and 4.2 V.¹⁰⁵ Cells charged to 4.4 V inconsistently perform well with higher retention, CE, and discharge capacity than 4.2 UCV and 4.0 UCV cells. The takeaways from these LCV and UCV experiments are being debated in the recent literature with some similar results but it was imperative to check these conditions for our unique system.^{20,89,105,106} Future work will try to optimize the electrolyte and Si electrode stability, specifically the binder, to eliminate the irreversible capacity loss encumbered by the phase transition at 3.25 V, and improve the cell retention from around 99.6 % per cycle to 99.9 % (57 cycle end-of-lifetime to 225 cycles, respectively) without sacrificing volumetric energy density.

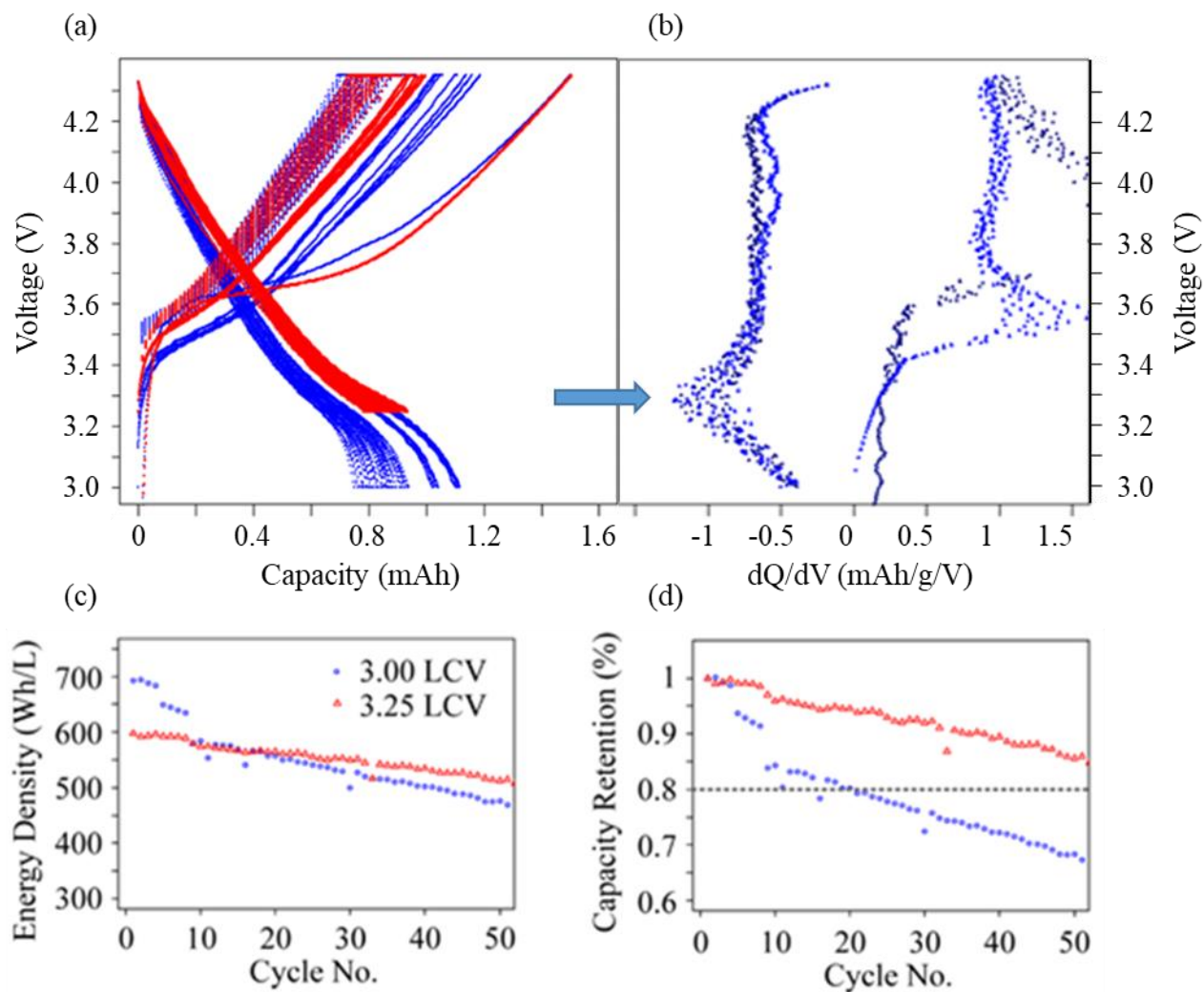
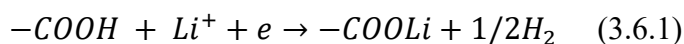


Figure 3.5.1. (a) Capacity vs. voltage profiles of NMC532||Si Composite full cells cycled at 320 mA g⁻¹ with either a 3.0 LCV (blue) or 3.25 LCV (red). (b) dQ dV⁻¹ plots of the first (navy) and second (blue) cycles of the NMC532||Si Composite full cell configuration. The blue arrow at approximately 3.25 V indicates the partly irreversible phase transition as silicon transitions from c-Li₁₅Si₄ to a-Li_xSi. (c) Plot of the energy density vs. cycle no. given by the discharge energy (Wh) divided by the total cell volume in liters (including the separator and both electrodes). (d) The capacity retention normalized to the initial discharge capacity during activation at 80 mA g⁻¹.

3.6. Characterization of Aqueous Binders for Silicon Electrodes

The choice of binder is more impactful in conversion- and alloying-based electrodes than in intercalation-based electrodes. Electroactive materials with minimal lattice strain, also known as topotactic materials, require a binder that crudely keeps the electrode together and attached to the current collector.⁶² However, electrodes that undergo conversion- and alloying-based reactions experience internal stresses that are magnitudes greater than their topotactic counterparts. For example, silicon expands by 320 % of its initial volume when fully lithiated to the $\text{Li}_{15}\text{Si}_4$ phase. Electroactive materials, like Si, which undergo significant stresses and volumetric expansion are consequently more prone to destabilization of the SEI layers as well as current collector delamination and electrode pulverization.¹⁰⁷ As a result, to improve the reversibility of high-stress electrodes, the binder needs to maintain the integrity of the electrode under demanding conditions and, in some cases, facilitate a more stable SEI.^{49,50,108}

The pertinent selection criteria for a binder includes: (1) crosslinking and functionalization, (2) ionic and electronic conductivity, (3) mechanical and adhesion properties, (4) water and electrolyte absorption, (5) crystallinity and melting point, (6) molecular weight, and (7) dissolution properties. These criteria determine the performance and implementation of the respective binder in an electrode architecture. An example of the first criteria is the condensation reaction that can occur between the carboxylic and hydroxyl groups of poly-acrylic acid (PAA) and SiO_x , respectively, as depicted in Figure 3.6.1. The PAA binder is further electrochemically reduced during the first cycle, forming a thin and protective SEI layer on Si.¹⁰⁹ The reaction that occurs as the carboxyl groups reduce is:



This reduction reaction contributes a thin SEI on Si surfaces while the condensation reaction can form a more brittle and inelastic electrode. This hypothesis is validated by experiments on thin films of dry aqueous binders.

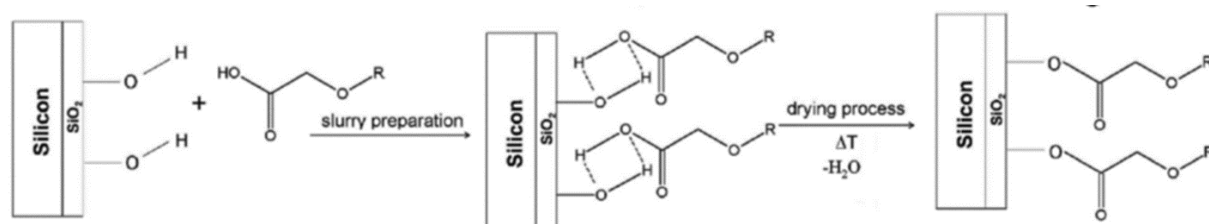


Figure 3.6.1. Depiction of the condensation reaction that occurs between poly(acrylic) acid and the hydroxyl groups in SiO_x to form a strong covalent bond between the two species.

Polymer blends are an appealing solution to create binders with better properties and performance than existing single-phase solutions. In these experiments, the weight ratio of PAA and SBR aqueous binder is varied in binary blended mixtures and thin film measurements of strength and swelling are conducted. The dry thin films shown in Figure 3.6.2 (a) vary significantly in tint and flexibility. While the PAA film is completely clear, transparent, and inflexible, the SBR film is extremely flexible and transparent with a yellow tint. The blended binary mixtures do not follow a strict linear progression between the two single-phase systems in regards to vary opaqueness and tint. The 80PAA:20SBR system has higher haze without any yellow hint, likely indicative of poor SBR dissociation. The thin film is capable of a 25 mm bending radius, as shown in Figure 3.6.2 (c). On the other hand, the 20PAA:80SBR blended system has streaks of yellow-tinted haziness with clear and transparent splotches. This is conversely, indicative of immiscibility of the co-polymer PAA with the aqueous SBR solution. Only the 50PAA:50SBR blended thin film shows good dissociation of both the PAA and SBR components into a single phase without any

noticeable separation of the mixture. The bending radius of the 50PAA:50SBR blend, as shown in Figure 3.6.2 (d), is < 5 mm, suitable for flexible electrode applications.

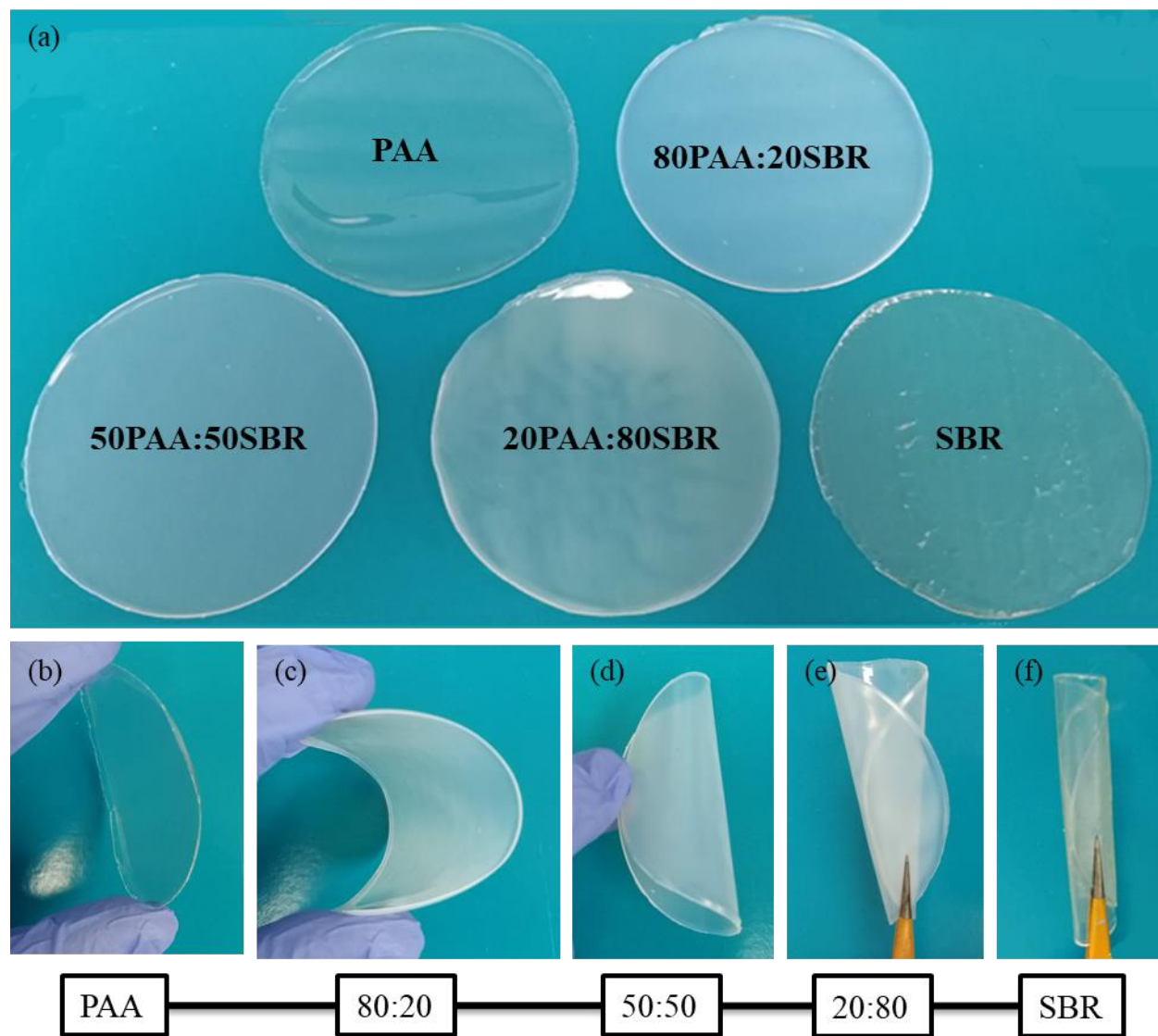


Figure 3.6.2. (a) Images of the single and binary binder thin films. The polymers are generally immiscible in the blended films except with equal weight of PAA and SBR (50PAA:50SBR). The flexibility of the thin films is shown in (b) through (f). The PAA thin film (b) is stiff and brittle relative to the SBR thin film (f).

The implications of these qualitative observations carry over into the mechanical stress-strain performance of a thin film systems, as seen in Figure 3.6.3. Not only are the optical

properties impacted by varying the weight ratio of PAA to SBR in blended mixtures, but the strength, swelling, and printing properties are as well. Binary blends with a majority of PAA chains by weight are a hard brittle plastic and offer high tensile strength (> 30 MPa) but minimal tensile strain (< 5 %) in thin film measurements. In comparison, blends with a majority of SBR elastomer are soft and offer lower tensile strength (< 15 MPa) with high tensile strain (> 400 %). However, the 50PAA:50SBR offers altogether different stress-strain performance with a yield point at 30.3 MPa and 11.4% strain that is followed by plastic strain hardening until fracture at 104.4% strain and ~ 28 MPa.^{110,111} This performance is indicative of a hard and tough polymer which balances the advantages of the SBR elastomer properties and the PAA brittle polymer properties.

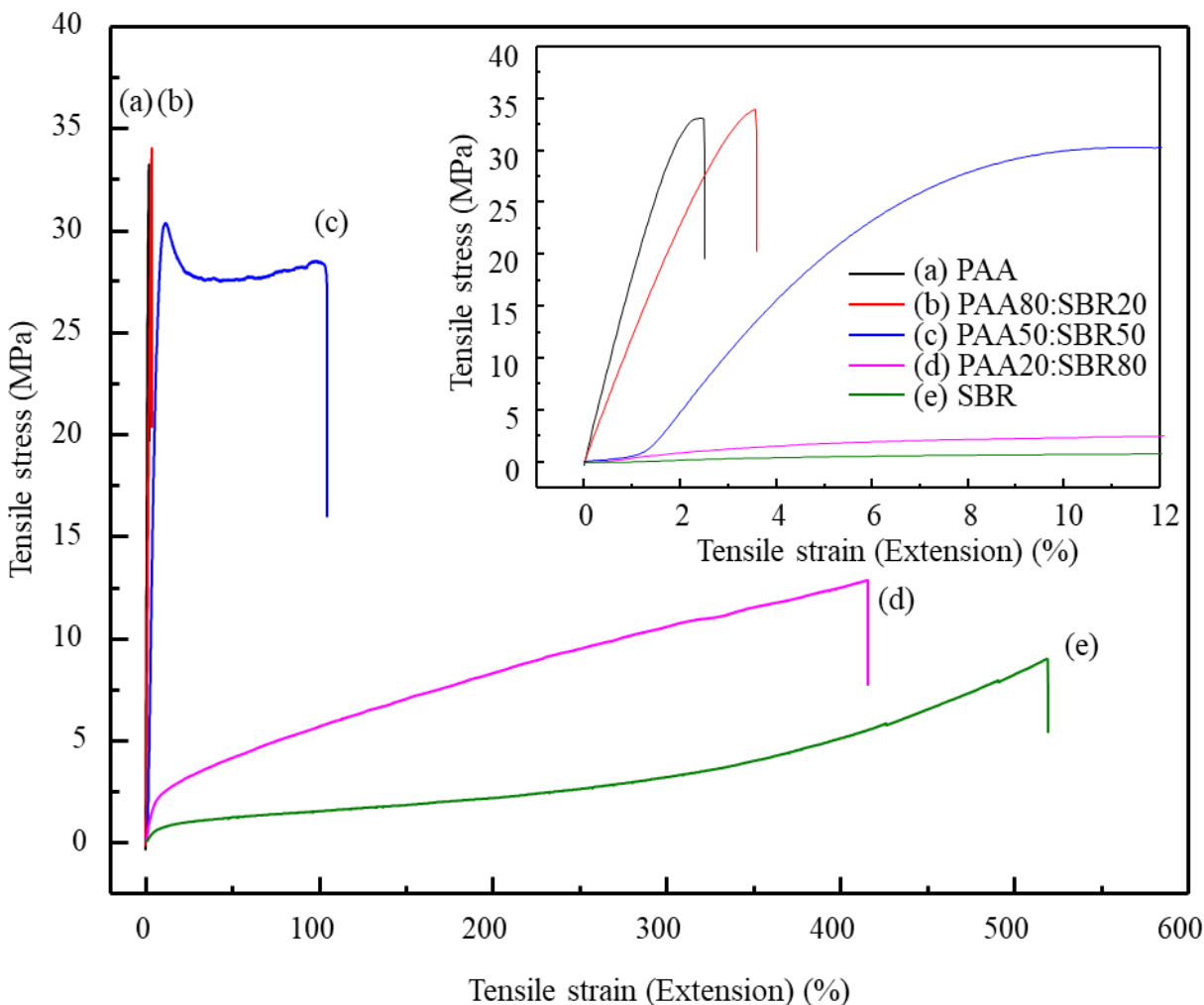


Figure 3.6.3. Stress-strain curves of the blended films of PAA and SBR. Curves (a) – (e) represent the performance of (a) PAA, (b) PAA80:SBR20, (c) PAA50:SBR50, (d) PAA20:SBR80, and (e) SBR films.

The swelling of the thin films is further investigated by immersing in distilled water for 24 hours at room temperature, as shown in Table 3.6.1 (a). PAA is known to be a rigid binder which forms hydrogen and/or covalent bonds in the electrode. Therefore, it is unsurprisingly that both PAA and the blended 80PAA:20SBR polymers experience 0 % volume change in this experiment. From these results, the 50PAA:50SBR blend swells 1.44 % in the aqueous solution while the pure SBR film which swells 3.33 %. Unfortunately, this does not fit a linear dependence that could hint

at the onset of better miscibility of SBR in PAA for a hard and tough polymer blend. These results already indicate that the performance of the 50PAA:50SBR polymer blend can be superior to a pure PAA-based binder. The next step is to check the electrochemical performance of the blended binders in Si-based electrodes.

Table 3.6.1. Thickness measurements of the PAAx:SBRy thin films before and after immersion in aqueous solution for 24 hours.

Samples	Thickness before (mm)	Thickness after (mm)	Volume change (%)
PAA	0.340	0.340	0
PAA80:SBR20	0.224	0.224	0
PAA50:SBR50	0.209	0.212	1.44
PAA20:SBR80	0.311	0.319	2.57
SBR	0.33	0.341	3.33

With the help of a colleague, Miaolun Jiao, a series of experiments to develop an aqueous binder for Si electrodes with better durability and electrochemical performance than neutralized poly-acrylic acid (Li-PAA) were proposed and implemented. The Si-based negative electrodes consist of 30 wt% functionalized silicon additive with partially reduced graphene oxide (f-Si-pRGO), which was described Section 3.1. The baseline electrode also contains 2 wt% carbon black, 58 wt% graphite powder and 10 wt% dry LiPAA binder in 1.5 – 2 wt% aqueous solution. The LiPAA solution is formed by neutralizing the unreacted carboxyl groups of PAA with lithium hydroxide (LiOH) until the pH reaches 6 - 7. This binder is specifically tested against the blended polymer system for better electrochemical performance in half cells and electrode fabrication.

Electrochemical tests including extended galvanostatic cycling, rate performance, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) are used to investigate the

electrochemical properties and performance of the blended binders. The impedance spectra and cyclic voltammograms in Figure 3.6.4 indicate variations in electrode conductivity with the choice of binder. After activation, the PAA60:SBR40 electrode is found to have the lowest charge transfer resistivity of around 15 Ω cm, including the SEI layer. This is noticeably less than the 60, 30, and 25 Ω cm charge transfer resistivity of the electrodes with PAA80:SBR20, CMC60:SBR40, and PAA binders, respectively. The cyclic voltammograms in the same half cell configurations indicate increasing stability of the Si composite electrodes with each additional cycle. The electrodes gradually activate due to the fast scan rate of the CV method, 0.1 mV/sec. A full activation cycle with lithiation to 0.01 V and delithiation to 1.5 V takes only 8 hours which is equivalent to a C/4 rate. This is extremely short compared to the $\geq$ C/20 rate which is the commercial standard to completely activate Si composite electrodes. Furthermore, the fast scan rate leads to large overpotentials for the lithiation and delithiation peaks on the CV curves and incomplete activation of the electroactive silicon material. The anodic peaks below indicate 0.4 V can be attributed to graphitic carbon and show strong reversibility with the cathodic peaks at 0.2 V and below. However, the anodic peak for α -Li_xSi_y delithiation at 0.5 V is highly polarized, especially compared to the typical delithiation plateau of Li₁₅Si₄ at approximately 0.4 V in the curves in Figure 3.6.5. Therefore, additional testing is performed to compare the performance of four binders.

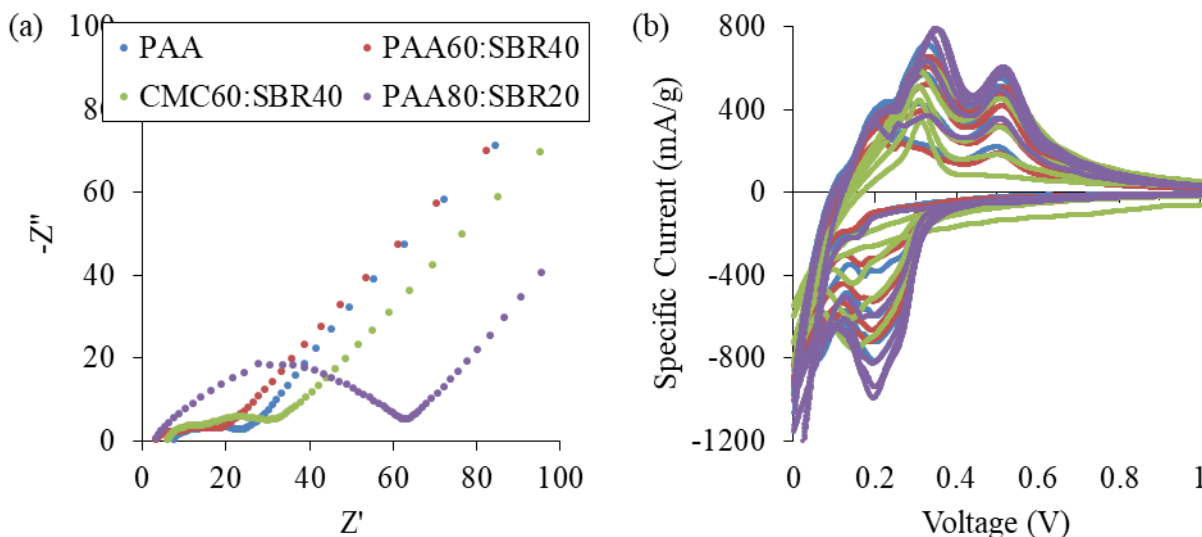


Figure 3.6.4. Impedance spectra and cyclic voltammetry of Si composite half cells with either PAA (blue), PAA60:SBR40 (red), CMC60:SBR40 (green), or PAA80SBR20 (purple) binder. The cyclic voltammograms and impedance spectra are normalized to the mass of the electrode.

Galvanostatic tests are conducted using a Biologic VMP3 or Arbin LBT system with CCCV protocol for rate and retention tests. Half cell configurations are activated three times between 0.01 – 1.5 V at C/20. In Figure 3.6.5, the lithation/delithiation curves of the cells during activation are given along with the ICE of each system. The Si composites in this study have a theoretical capacity of 1232 mAh g⁻¹, assuming 10 wt% pRGO in the Si additive from TGA results. During activation the PAA electrode reaches 89.7 % of its theoretical capacity while the PAA60:SBR40 reaches 84.9 %, the PAA80:SBR20 reaches 82.9 %, and the CMC60:SBR40 reaches 89.6 % of its theoretical capacity. This result strongly correlates to the ICE of the electrodes but not the mass loading of the electrodes. Cells with a higher ICE also have better electrode utilization during activation. This can be attributed to the amount of inactive silicon oxide produced during the aqueous slurry mixing and coating. Therefore, the lower activation of the PAA:SBR systems is attributed to the 21 – 25 % of silicon nanoparticles that do not contribute to

the reversible electrode capacity while the PAA and CMC:SBR systems only have 15 % inactive Si. By further lithiating down to 0.005 V with more extended CV protocol, more of the electrode could be activated, but that does not necessarily lead to better cycling retention or rate performance as evidenced by the results in Figures 3.6.5 and 3.6.6. The ICE and activation of electrodes in Figure 3.6.6 for retention tests demonstrate the inconsistency of these metrics between electrodes from the same batch with the same binder. Both the ICE and initial capacity do not strongly correlate to the binder as much as the electrode processing conditions and silicon activity in particular samples.

Both the PAA60:SBR40 and PAA electrodes fully lithiate to the $c\text{-Li}_{15}\text{Si}_4$ phase below 60 mV because of their low electrode resistance, as evidenced from the impedance curves in Figure 3.6.5. However, at higher rates each cell undergoes lithiation and delithiation into $\alpha\text{-Li}_x\text{Si}$ and $\alpha\text{-Si}$, respectively. This amorphous cycling of silicon has two signatures at $x = 2.0$ and 3.5 in $\alpha\text{-Li}_x\text{Si}$ which occurs at 250 and 100 mV, respectively.¹¹² The former is associated with the formation of large clusters from the $\alpha\text{-Si}$ structures which are broken into small cluster, Si-Si dimers, and, eventually, isolated Si atoms in the later.¹¹³ The two transitions are found to be kinetically limited, meaning that under dense or tortuous electrode structures, lithium ions will continue to react with $\alpha\text{-Li}_x\text{Si}$ on surfaces to form $x = 3.5$ to the exclusion of more thorough lithiation to $x = 2.0$, underneath the surface.¹¹⁴ As a result, even after transient SEI formation and particle expansion is mediated in the first 30 to 60 cycles, the lithiation capacity of the electrode is lost due to the formation of inaccessible Si within kinetically impeded particles and tortuous structures.^{113,89,115}

By reducing particle size and avoiding the crystalline phase transition, the reversibility of the Si composite can be improved albeit at the expense of greater SEI formation.^{25,116} The highly anisotropic volume expansion to $\text{Li}_{15}\text{Si}_4$ results in large lithiation-induced stresses with a high

likelihood of particle fracture, for diameters larger than 150 nm, and irreversible lithium trapping.¹¹⁷ The cycling of amorphous silicon can be further engineered by the cutoff potentials and parameters of the CCCV protocol. As discussed in section 3.5, the half cell performance is greatly dictated by the lithiation and delithiation of the silicon. The amorphous cycling of Si additive in the composite systems in Figures 3.6.5 and 3.6.6 lead to good performance.

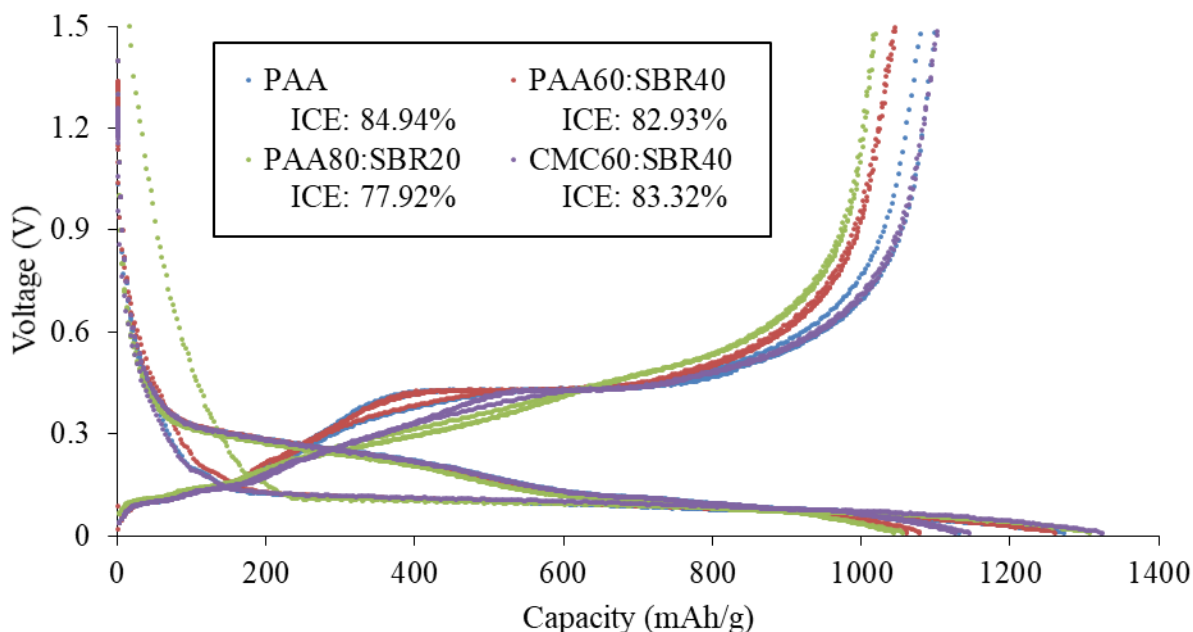


Figure 3.6.5. First two activation cycles of the Si composite half cells with either PAA (blue), PAA60:SBR40 (red), CMC60:SBR40 (green), or PAA80SBR20 (purple) binder between 0.01 – 1.5 V at C/20 rate. The capacity is normalized to the mass of the electrode.

The capacity retention and coulombic efficiency of the cells after 200 cycles at C/5 is given in Figure 3.6.6, below. The capacity retention of the PAA60:SBR40 electrode is noticeably better than the CMC:SBR and other binder systems in Figure 3.6.6 (b). After activating the cell, the PAA60:SBR electrode maintains 53% of its initial reversible capacity with 99.41 % CE and 99.75 % retained capacity per cycle at C/5. Looking at the coulombic efficiency of the cell in Figure 3.6.6 (c), it becomes more apparent, why the PAA60:SBR40 binder outperformed the other

systems. While the PAA electrode has high coulombic efficiencies starting at 99.5 % in the initial transient cycles, the CE decreases over time. This decrease in CE over 65 cycles corresponds closely with the permanent expansion of the nanoparticles into porous and amorphous silicon, as described in previous work by Wetjen, *et al.*⁸⁹ In contrast, the CMC:SBR cell has low transient coulombic efficiencies around 98.2 % which gradually increases over time. The PAA60:SBR40 is an ideal compromise between the pure PAA and CMC:SBR systems. Its transient CE is 99.0 % but gradually improves over time. This is manifested in the capacity retention of the cell and indicates less SEI formation and particle detachment. The PAA:SBR system with 60:40 wt ratio also performs significantly better than the 80:20 system in cycling retention and coulombic efficiency. This indicates that the polymer blend with both hard and tough mechanical properties performs better than the 80:20 blend which shares many of the same brittle characteristics of the pure PAA system, with less carboxyl and hydroxyl groups to attach to the SiO_x surface. In this study, a blended binder is proposed with improved properties over two industry standards, PAA and CMC:SBR. The composition of the blended system is characterized in polymer thin films before conducting electrochemical tests. The engineering of a hard and tough composition results in the best performance in half cell configurations.

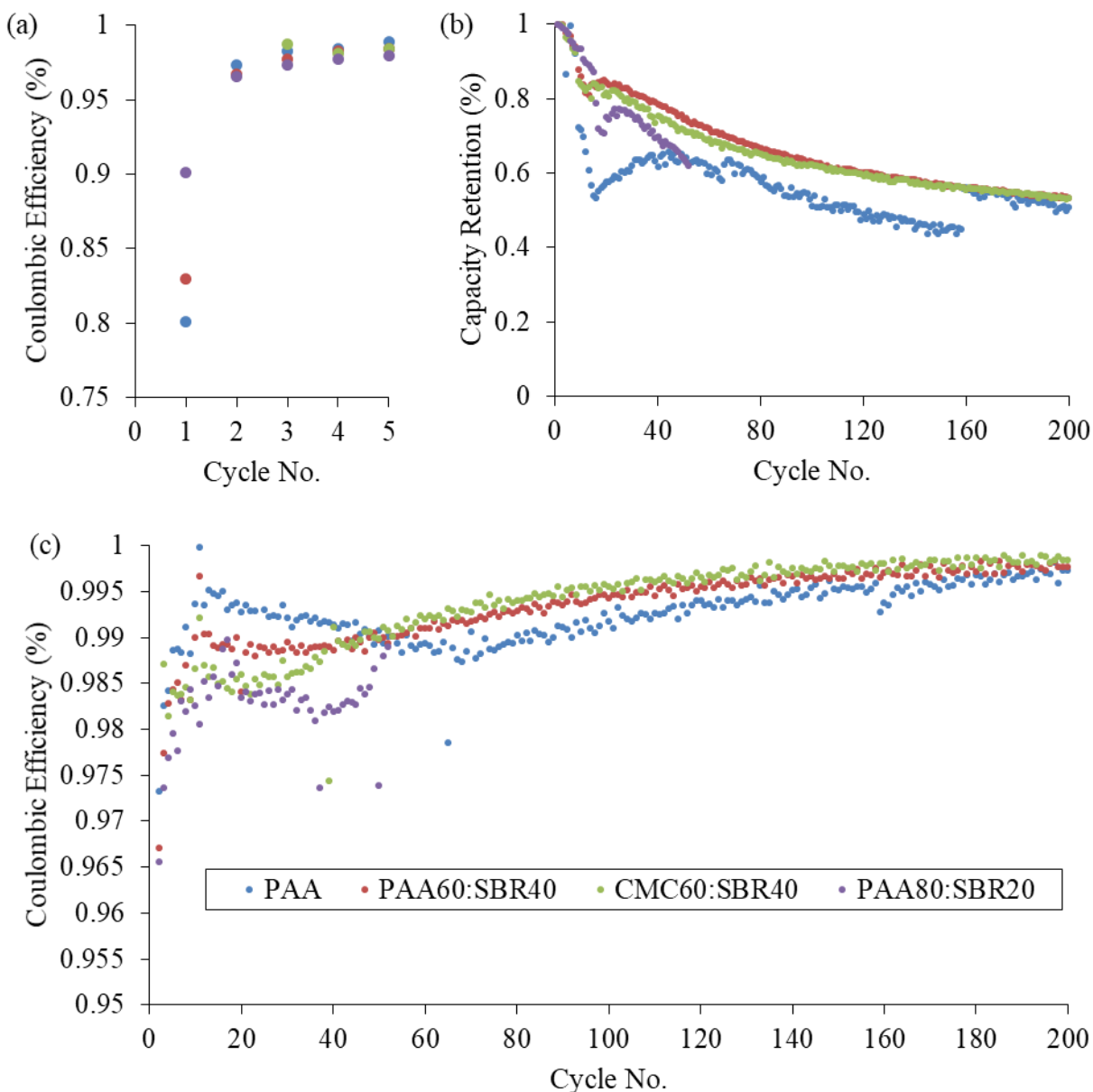


Figure 3.6.6. Plots of the (a) initial or transient coulombic efficiency, (b) capacity retention, and (c) stabilized coulombic efficiency of Si composite half cells with either PAA (blue), PAA60:SBR40 (red), CMC60:SBR40 (green), or PAA80:SBR20 (purple) binder. Cells are activated three times between 0.01 – 1.5 V at C/20 before cycling three cycles at C/10, two cycles at C/5, two cycles at C/2 and then extended cycling at C/5. The coulombic efficiency is defined as the delithiation capacity divided by the lithiation capacity of the respective cycle.

3.7. Flexible and Thin Lithium Ion Pouch Cells

The wearable tech market is expected to grow to \$100 billion by 2024 as smartwatches, fitness trackers, hearables, medical devices and smart clothing gain traction across a number of industries.¹¹⁸ Flexible, thin, and safe lithium ion batteries are a core technology to enable wearable devices but few state-of-the-art systems can deliver in every performance metric. Current efforts require a multidisciplinary approach to incorporate novel materials with improved energy density and electrochemical performance into safe and flexible packages that are often use-specific. In this work, lithium ion batteries with a gel polymer electrolyte are manufactured by roll-to-roll compatible processes for applications requiring high energy-density and high flexibility in an ultrathin cell format.

Kapton polyimide films are a strong, thermally and chemically stable material which serve as a moisture barrier for various characterization methods. Three forms of Kapton tape were procured and tested to evaluate thin and flexible current collector and inner packaging layers for the proposed system. The 120FN616 tape was determined to be the most suitable current collector substrate and packaging layer because it (a) has a heat bondable layer, (b) is moisture and chemical resistant, (c) is 25 μm thick, and (d) has good impact and tear strength. A table of the key properties of Kapton 120FN616 tape is included below from the product sheet. A picture of the LFP cathode screen-printed on a Kapton tape current collector is included in Figure 3.7.1 (a). The current collector is first electron-beam (e-beam) coated with a thin (60 μm) layer of titanium as an adhesive, followed by a thicker layer of Cu or Al for the anode and cathode current collectors, respectively. A mask is used to print a 1.5 x 1.5 inch area and a 0.5 inch tab by e-beam deposition. The electrode slurry is prepared by mixing the components in a mortar and pestle similar to the methods outlined in Section 3.1. The negative and positive electrodes both

consist of 8:1:1 ratios between the electroactive material, carbon black additive, and the dry weight of binder (PVDF or Sodium Alginate for the cathode and anode, respectively). An image of the full cell after assembly is given in Figure 3.7.1 (b). A variation of the design is shown in Figure 3.7.1 (c) which includes an additional polymer sealant and conventional electrodes coated on stand-alone metal current collectors.

Table 3.7.1. The properties and test methods of the multi-layer Kapton 120FN616 polyimide, heat-sealing tape.

Property	120FN616 (at 23 °C)	Test Method
Ultimate Tensile Strength	207 MPa	ASTM D882, Method A
Yield Point at 3%	61 MPa	ASTM D882
Ultimate Elongation	75 %	ASTM D882
Impact Strength	78 N·cm	DuPont Pneumatic Impact Test
Tear Strength, initial Graves	1.8 N	ASTM 1004
Density	1.53 g/cc	ASTM 1505
Dielectric Constant	3.1	ASTM D150
Volume Resistivity	$1.4 \times 10^{17} \Omega \cdot \text{cm}$	ASTM D257
Water Vapor Permeability	1.13 g/(100 in ² ·24hr)	ASTM E96

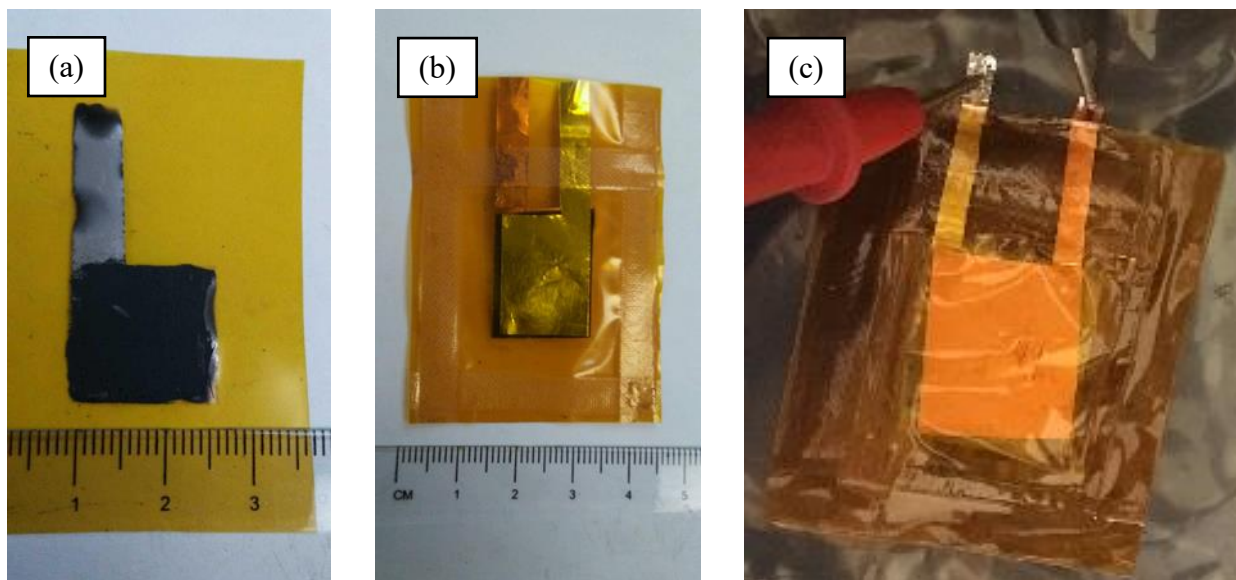


Figure 3.7.1. (a) Image of a 1.5 x 1.5 inch LFP cathode screen-printed on a Ti|Al e-beam-coated Kapton substrate. (b) Image of the thin and flexible full cell which uses the 120FN616 tape as both a heat-sealable package and a current collector substrate. (c) Image of the thin and flexible design using additional polymer sealant layers and standalone metal tabs.

To avoid issues related to delamination and cracking of the electrodes, topotactic lithium iron phosphate (LFP) cathodes and graphite (Gr) anodes are selected as the energy-dense electroactive materials in this study. The olivine structure of LFP operates as a one-dimensional conductor of Li ions along the [010] direction. As the cathode delithiates, the structure undergoes a two-phase transition in which the oxidation state of Fe^{2+} ions at the octahedral sites change to Fe^{3+} . LFP is made of cheaply sourced materials with higher thermal stability and minimal capacity fade during full depth-of-discharge (DOD), extended cycling. This makes it an excellent material for applications that prioritize price and long term stability over energy density. The LFP used in this work are nanoparticles coated with conductive carbon to overcome the inherent low Li-ion diffusion coefficient (10^{-14} - 10^{-15} cm^2/S) and electric conductivity (10^{-9} - 10^{-10} S/cm) of the bulk material.¹¹⁹ Both natural and synthetic graphite are also intercalation-based materials with

low volume expansion (< 10%) and high stability for extended cycling with full DOD. In this study, synthetic graphite is received from Sigma Aldrich and used as the negative electrode electroactive material with sodium alginate (10 wt%) and carbon black additive (CB) (10 wt%).

The gel electrolyte consists of a porous PVDF-HFP polymer host with nano- Al_2O_3 fillers and organic liquid electrolyte of composition 1.0 M LiPF_6 in EC:DEC (50:50 wt%). The polymer host is fabricated by mixing PVDF-HFP and nano- Al_2O_3 in acetone for 24 hours and then solution casting on a glass substrate. The porosity and thickness of the host are defined by the concentration, solvent, drying method, and surface area. These parameters are controlled to achieve a film with approximately 40% porosity, as determined by SEM, and 15 μm thickness. The conductivity of the gel electrolyte is 3×10^{-4} S/cm in a symmetric cell. The electrode slurries are prepared by mixing in a mortar and pestle before screen printing on 4 cm^2 area of the Kapton tape substrates. A mask ensures that the electrode coats the e-beam current collector uniformly. After drying at 105 $^\circ\text{C}$ in a vacuum oven overnight, the negative electrode is laminated first with the dry polymer host, followed by the positive electrode. After sealing three sides, 25 $\mu\text{L cm}^{-2}$ electrolyte is added to the Kapton pouch cell and the final edge is sealed with an additional polymer sealant. The thickness of the pouch cell is listed in Table 3.7.2.

Table 3.7.2. The stacking thickness of the ultrathin and flexible, single layer LFP||Gr battery.

Flexible and Thin Battery Layers	Thickness (μm)
Heat-sealable Kapton 120FN616	25
Ti/Cu e-beam-coated current collector	0.25
Graphite:CB:Sodium Alginate (8:1:1) negative electrode	35
Gel polymer electrolyte	15
LFP:CB:PVDF (8:1:1) positive electrode	53

Ti/Al e-beam-coated current collector	0.25
Heat-sealable Kapton 120FN616	25
SUM	153.5

The rate performance of the LFP||Gr full cells cycled between 2.8 – 3.9 V is shown in Figure 3.7.2 (a). After forming a stable SEI on the graphite electrode at C/20, the full cell retains 97.0 % of its capacity at C/5, 90.0 % at 1C and 78.2 % at 2C, which corresponds to 1.01 mA cm⁻² or 340 mA g⁻¹. Differential capacity analysis (dQ dV⁻¹) of the full cell shows stable intercalation stages in and out of the graphite electrode at C/20 and C/5. At higher rates, the delineation of the 4 binary (Li_xC₆) phase transitions also seen in Figure 3.7.2 (b). The dQ dV⁻¹ curves at C/20 and 2C rates, reveal 140 mV of hysteresis of the stage II to III transition, also corresponding to x = 0.5 and 0.33 in Li_xC₆ during the delithiation process, respectively. This corresponds to a 165 mV average voltage loss in the full cell at a 1C discharge rate. By switching to a higher grade of active materials and hot-roll pressing the electrodes, higher capacity retention could be achieved as evidenced by previous work in Section 3.3 and 3.4.¹²⁰

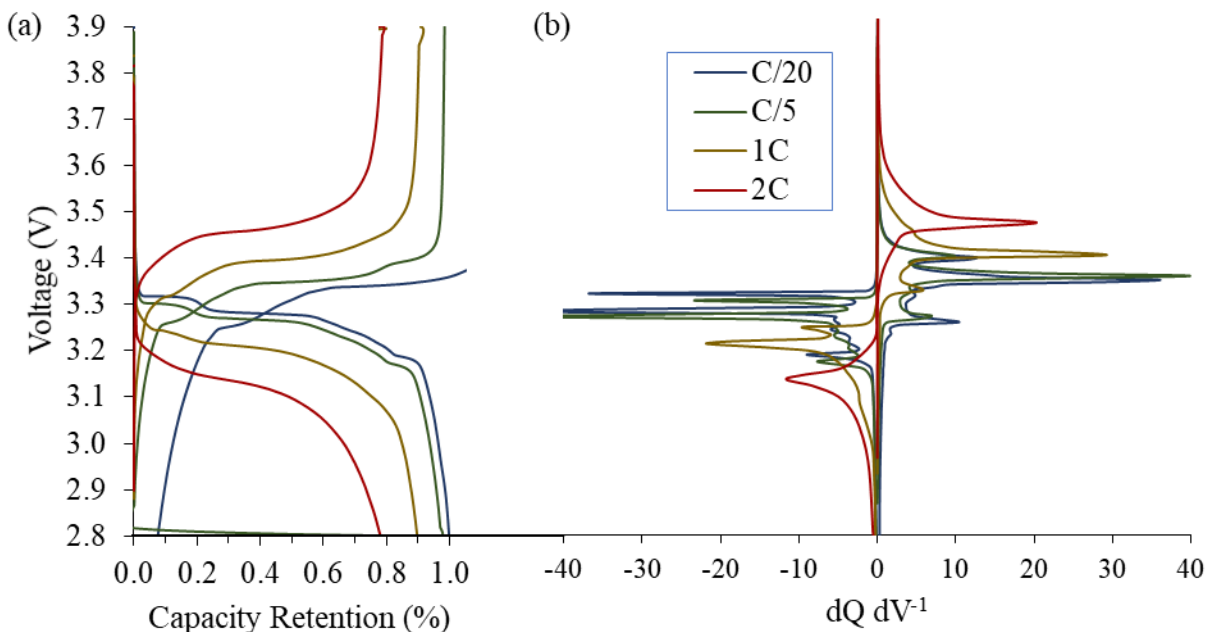


Figure 3.7.2. (a) Voltage vs. capacity retention of the LFP||Gr pouch cell at C/20 (blue), C/5 (green), 1C (yellow), and 2C (red). (b) Differential capacity analysis of the pouch cells.

Looking at the long-term cycling performance in Figure 3.7.3, the same full cell achieves 99.74 % and 99.82 % average coulombic efficiency (CE) after 90 and 1000 cycles at 2C, respectively. However, the initial coulombic efficiency (ICE) of the cell is only 75.4 %. This is indicative of the high surface area of the $\leq 20 \mu\text{m}$ artificial graphite from Sigma Aldrich which is better suited to supercapacitor applications and graphene synthesis than high efficiency lithium ion batteries. The full cell still manages to retain 68.9% of its capacity after 100 cycles and 62.1% after over 1000 cycles to full DOD between 2.8 – 3.9 V. This corresponds to 0.957 mAh of capacity or 3.011 mWh of energy after full discharge. The average voltage of the full cell slips 0.75 % or 25 mV from the 15th cycle, the first cycle at 2C, to the 1018th cycle at the same rate.

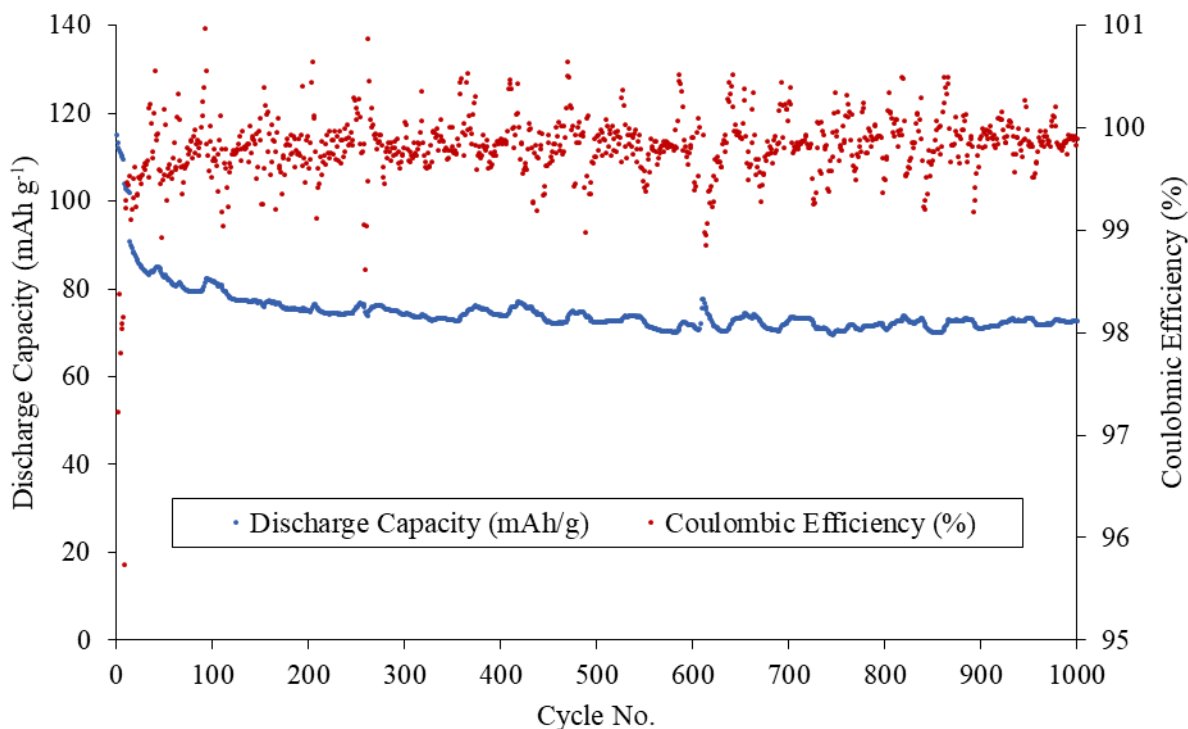


Figure 3.7.3. (a) Extended galvanostatic cycling of the LFP||Gr pouch cell with 4 cm² active area up to 2C rate, equivalently 1.01 mA cm⁻² or 340 mA g⁻¹. The average CE at 2C is 99.82 %, the ICE is 75.4 %, and the average discharge voltage during the first cycle is 3.25 V.

In this study, thin and flexible pouch cells were designed and fabricated using heat-sealable Kapton tape substrates, LFP cathodes, and Gr anodes. The cells retained 80.0 % of their capacity after 430 cycles at 2C and 78.6 % after 1000 cycles, normalized to the first cycle at 2C. The rate performance and hysteresis of the cells is also evaluated by differential capacity analysis. The full cell energy density of the single layer LFP||Gr cell including all inactive components is 73 Wh L⁻¹. Additional images and bending videos of the full cell are attached in the supporting information. In subsequent studies, the safe and thin gel polymer electrolyte is printed directly on later generations of the flexible and thin lithium ion batteries with mixed ionic

liquid electrolyte. This work provided a baseline for further investigating novel electrolyte systems for energy-dense lithium ion batteries.

Chapter 4: Electrolyte Systems for Silicon-based Full Cells

Lithium ion batteries (LIBs) have become a pillar of modern technology although they contain numerous reactive and hazardous components that can catastrophically fail under seemingly benign conditions. One of the largest safety concerns of commercial LIBs is associated with thermal runaway which can result in violent explosions and fires that are not easily put out. This risk is shown to be compounded in some cells demonstrating high-capacity chemistries, such as silicon-based negative electrodes tested by the SNL Battery Abuse Testing Laboratory (BATLAB).^{98,99} One approach to reduce the risk associated with thermal runaway is partially or fully substituting the flammable hydrocarbons for other solvents which can provide comparable ionic conduction between the positive and negative electrode. Three systems are presented in this chapter and listed in table 4.1 to replace the baseline carbonate-based electrolyte for energy-dense LIBs. A major deliverable of the renewed collaborative project with Analog Devices Incorporated (ADI) is to develop a more robust nonflammable electrolyte that minimizes the threat of catastrophic failure.

Table 4.1. Electrolyte systems tested for energy dense lithium ion batteries.

System	Motivation	Conclusions	Tailored Compositions
Additives in Organic Electrolyte	1. Screen and identify additives that are worth testing in the nonflammable electrolytes.	- Promising initial result from DEPC additive. Will test in future electrolyte formulations. - DTD purity as received was poor, resulted in inconclusive results	1M LiPF ₆ in EC:DEC (50:50 wt ratio) baseline a) 10 wt% FEC + 1 wt% VC b) 5 vol% DEPC c) 5 vol% DEPC + 1 wt% DTD + 5 vol% FEC d) 1 wt% DTD + 5 vol% FEC
Mixed Ionic Liquid Electrolyte	1. High temperature stability	Flammable with slightly better thermal stability	a) PYR ₁₃ TFSI:EC:DEC:VC (40:29:29:2 vol%) + 0.58 M

	2. Nonflammable ionic liquid component	Poor SEI formation and retention in our system.	LiPF ₆ + 0.15 M LiBOB b) 13 other compositions tested
Sulfonated Electrolyte (ARL collaboration)	1. Nonflammable 2. Suitable for high voltage spinel cathodes 3. Forms an anion-based SEI with unique properties	- Nonflammable - Poor wetting on PP separators - Poor SEI formation and retention in our system. - Suitable for high voltage spinel cathodes - Forms an anion-based SEI with unique properties	a. 3.0m LiFSI in SL b. 3.0m LiFSI in SL + 2 wt% VC c. 3.5m LiFSI in SL d. 2.0m LiFSI in SL
Fluorinated Electrolyte (ARL collaboration)	1. High flash point and self-extinguishing solvents 2. Fluorine-rich SEI with FEC	- Flame Retardant <i>Developed a less-expensive system</i> using DMC solvent - Screening additives and gradually seeing improvements - Promising initial results but SEI does not completely survive the repeated volume expansion of Si@Graphene.	a. 1m LiPF ₆ in HFE:FEC:DMC (2:2:6 wt%) + 3wt% LiDFOB b. 1m LiPF ₆ in FEC:FEMC:HFE (2:6:2) c. 1m LiPF ₆ in FEC:FEMC:HFE w/ 1 wt% LiBOB (anion-based SEI former)

4.1. Mixed Ionic Liquid Electrolyte

This section details the design and implementation of a novel, mixed ionic liquid (MIL) consisting of PYR₁₃TFSI:ethylene carbonate:diethyl carbonate:vinylene carbonate (40:29:29:2 vol%) with 0.58 M LiPF₆ and 0.15 M LiBOB for phase I of the flexible battery project. The properties of the MIL solvents tested during this study are included in Table 4.1.1 below. Ionic liquids are salts with sub-room temperature melting points which can provide non-flammability,

good anodic and cathodic stability, low toxicity, high thermal stability, extremely low vapor pressures, and high ion content. Room temperature ionic liquids have melting points below 100°C due to weak coordination between the anions and organic cations.^{121,122} Two commonly studied anions for Li salts in LIBs and room temperature ionic liquids are bis(trifluoromethanesulfonyl)imide (TFSI⁻) and bis(fluoromethanesulfonyl)imide (FSI⁻). TFSI⁻ is selected in this work due to its performance in previously demonstrated systems, thermal stability, and lower cost than FSI.^{123–125} In particular, although FSI anions are known to display higher conductivity than even PF₆, they are also less thermally stable than TFSI anions. However, without additional additives to form a passivating AlF₃ interface on the Al current collector, the TFSI anion is known to corrode Al above the pitting potential, E_p, or approximately 3.4 V.^{126,127} This issue is mediated in some works by the addition of FSI anions, LiPF₆, or LiBOB to the baseline N-propyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₃TFSI) system. In this study, LiPF₆ salt is added with carbonate co-solvents to mediate the high viscosity of the TFSI⁻ based ionic liquid and Al corrosion. Additionally, the polymeric SEI former, VC is added to form a more stable and effective interface.¹²⁸

Table 4.1.1. Properties of the solvents in the final MIL system.

Solvent	MW	T _m (°C)	T _b (°C)	T _f (°C)	η (cP)	ε _r	ρ (g/cc)	Molecular Structure
EC	88.1	36.4	248	160	1.85 (40°C)	89.78 (25°C)	1.32	Cyclic
PC	102.1	-48.8	242	132	2.53 (30°C)	64.92 (25°C)	1.2	Cyclic
DEC	118.1	-74.3	126	31	0.585 (25°C)	3.12 (25°C)	0.97	Linear
DMC	90.1	4.6	91	18	0.748 (25°C)	2.82	1.06	Linear
FEC	106	23	212	102	4.1	106	1.454	Cyclic

PYR ₁₃ ⁻ TFSI	PYR ₁₃ ⁻ 408.4	10	T _d - 417	-	71.23 (25°C)	-	1.44	Cyclic cation
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Ionic liquids based on quaternary ammonium cations such as pyrrolidinium (PYR⁺) with commercial Li salts have high electrochemical stability up to 5.9 V vs. Li⁺/Li, high thermal stability, and feasible ionic conductivities for commercial LIBs. The primary hurdles for PYR⁺-based electrolytes pertain to the solution viscosity and interface formation even though the nonflammable, ionic liquid only constitutes 40 vol% of the final electrolyte system. To cycle at room temperature, PYR₁₃TFSI ionic liquids require co-solvents to lower the viscosity from 61 cP and thereby raise the conductivity.¹²⁹ However, even with a high ionic conductivity, electrode and separator wetting can be limiting factors in viscous systems with compact electrodes. In preliminary tests without carbonate co-solvents, the PYR₁₃TFSI ionic liquid does not wet the interface of NMC and Si composite electrodes without additional steps to fully activate the electrode.¹³⁰ Co-solvents and additives are also critical for forming stable interfaces with graphite electrodes. The PYR cation can intercalate into graphite carbon at low potentials and irreversibly exfoliate the anode without forming a passivating SEI. After testing over a dozen recipes, VC and LiBOB additives are down-selected to enable stable SEI formation on Si composite electrodes with electroactive graphite. By mixing the PYR₁₃TFSI with carbonate co-solvents and additives, MIL electrolytes can perform better for lithium ion systems and form stable interfaces without Al corrosion.^{131,132,124,133,134,125}

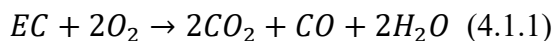
In this study, room temperature ionic liquid is partially blended with a baseline organic electrolyte, 1M LiPF₆ in EC:DEC (50:50 wt%), to passivate the Al and graphite interfaces and lower the viscosity. Previous reports claim retained flame retardant and even non-flammable properties of MIL systems with similar chemistry or at least 40 vol% ionic liquid.^{124,133} In thorough

safety tests on the blended electrolyte system, our work shows these properties are overstated. The MIL electrolyte with 40 vol% ionic liquid is no longer flame retardant or nonflammable, although it does demonstrate delayed combustion under a free flame, as shown in Figure 4.1.1. Nevertheless, the MIL electrolyte is tailored for pouch cells with high Ni-content cathodes, i.e. NMC811, and Si composite anodes. Additional safety tests demonstrate low rates of catastrophic failure of the tailored system in over-charge puncture and bend tests with pouch cell configurations.

The performance of the final MIL electrolyte is given by the cyclic voltammograms and cycling performance using NMC811 (C018), NMC532 (C015), and Si composite (A011) electrodes from the ANL CAMP facility. The CV of the NMC811||Si composite full cell in Figure 4.1.1 (a) shows minimal peak deviation after the first cycle. However, there are two phase transitions in the voltage window, which require cautious interpretation without a third reference electrode, but can be understood within the context of previous studies on NMC811||Gr and NMC811||Li cells. NMC811 is tested with the MIL system due to the economic advantages to reducing Co content in cathode materials and the high theoretical capacity. However, the observed phase transitions of NMC materials add considerable conflicting factors that not only impact high Ni-content cathodes, but also constrain the UCV of NMC full cells.^{135–137} In the 2nd charge step of the NC811 system, two anodic peaks are observed. One anodic peak at 3.6 V which continues into a separate peak at 4.25 V. This first peak belongs to both lithium alloying with Si in the anode and the NMC phase transition from a hexagonal to a monoclinic ($H1 \rightarrow M$) lattice. These reliable and reversible transitions are also observed in the NMC532 cell in Figure 4.1.1. (b). In the NMC532 cell the current drops precipitously after that anodic peak, and in the literature, additional transitions from $M \rightarrow H2$ and $H2 \rightarrow H3$ do not occur until higher cutoff potentials around 4.4 V

for any stoichiometry between 111 – 622 which were only recently reported by studies with UCVs up to 4.8 V.

In the NMC811 cell with the Si-based anode, the $M \rightarrow H2$ and $H2 \rightarrow H3$ phase transitions occur in quick succession at ~ 3.95 V and 4.15 V, respectively, with the second resulting in a large anodic feature. The second, larger feature is of particular importance as an oxygen redox feature. This $H2 \rightarrow H3$ phase transition is associated with oxygen redox due to the release of oxygen of various NMC compositions delithiated to 80-90% state-of-charge in previous gas analysis and on-line electrochemical mass spectrometry (OEMS) studies. These studies find a sharp increase in O_2 evolutions at the same potentials as the $H2 \rightarrow H3$ phase transition in NMC cathodes. This O_2 evolution is also synonymous with changes in CO_2 and CO evolution rates associated with chemical oxidation of the electrode rather than electrochemical oxidation of electrolyte. Electrochemical oxidation is distinctly different and attributed to the electro-oxidation of EC to CO or CO_2 and protic species ($R-H^+$) which increase electrolyte acidity. This is separate from chemical oxidation which occurs at the cathode surface are results in a discrete surface transformation from the layered NMC H3 (MO_2) structure to a spinel (M_3O_4) and, eventually, rock salt phase (MO) structures with the release of reactive oxygen species ($^1O_2$). One proposed mechanism, (Equation 4.1.1) from the Gasteiger group in collaboration with BMW AG, for the reaction of EC solvent with reactive oxygen species is given below:



The $H2 \rightarrow H3$ phase transition and oxygen redox reaction significantly limits the reversible, working voltage window of NMC811 cells. Speculation as to the structural origin of the $H2 \rightarrow H3$ phase transition is rooted in previous work on NMC111 cathodes.^{136,138} Delithiation of NMC111 by 2/3 leads to a measurable increase in the c-parameter of the layered structure which

is attributed to coulombic repulsion between negatively charged oxygen layers. However, at the $H2 \rightarrow H3$ transition with $> 80\%$ delithiation, the c-parameter shrinks as new covalency between lattice oxygen and metal cations propagates. This oxidation of the oxygen anions in the layered structure was similarly observed by *in-situ* XRD for the parent cathode $Li_{1-x}NiO_2$ (LNO).¹³⁹ In order to avoid this transition, NMC811 cannot be stably cycled much above 4.0 V, which significantly limits the theoretical energy density of NMC811 full cells relative to NMC532 and NMC622 cells with 4.3 V UCVs. After taking into account the additional capacity faded associated with the less anodically stable NMC811, future studies focused on full cells with NMC532 cathodes.

The full cell from Figure 4.1.1 (c) is cycled in a pouch cell first at C/20 for 2 cycles, then at C/10 for 5 cycles, and finally at C/5 until failure. Inset is the coulombic efficiency of the cell during the first 24 cycles at C/5. Although the retention of the cell is nearly 80% after 50 cycles at C/5, the coulombic efficiency only rises above 99.0 % after the full activation process at C/20 and C/10. Furthermore, the coulombic efficiency remains under 99.5 % for the full duration of the cycling test. This most likely indicates poor SEI formation of the MIL electrolyte on the expanding and contracting Si nanoparticles.

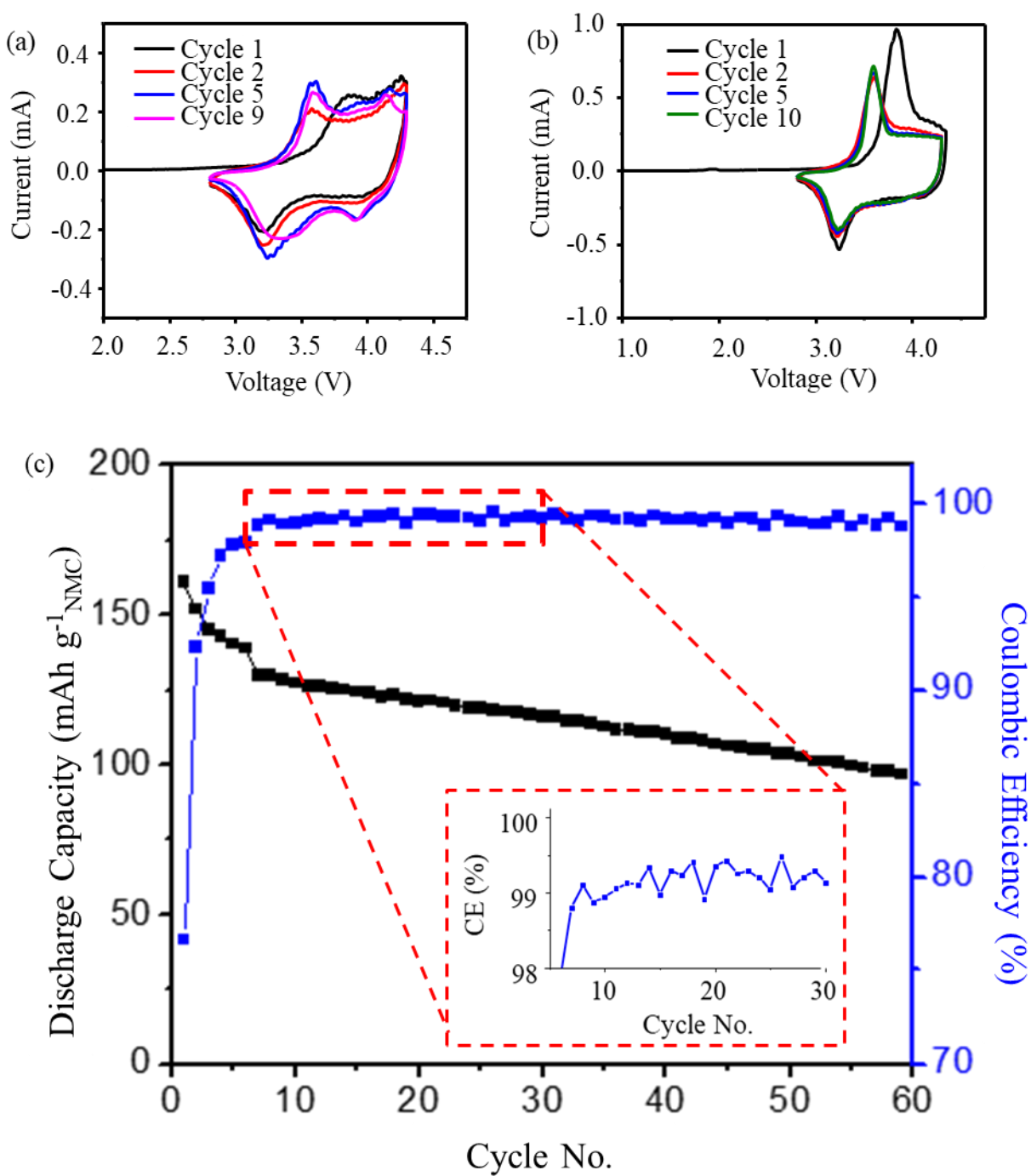


Figure 4.1.1. Cyclic voltammetry of the $\text{PYR}_{13}\text{TFSI}:\text{EC}:\text{DEC}:\text{VC}$ (40:29:29:2 vol%) + 0.58 M LiPF_6 + 0.15 M LiBOB MIL electrolyte with (a) NMC811 and (b) NMC532 positive electrodes

against Si composite negative electrodes. (b) Galvanostatic cycling between 4.3 – 3.0 V of the same electrolyte system with NMC532||Si composite electrodes.

The impedance spectra of uncharged NMC811|Si Composite full cells with the MIL electrolyte (blue) and organic control electrolyte (red) are shown in Figure 4.1.2 (a). The charge transfer resistance prior to cycling is less than $20 \Omega \text{ cm}^{-2}$, similar to the negative electrode in half-cell measurements. Figure 4.1.2 (b) shows the cycling retention of the 811NMC||Si full cells. Relative to the 811NMC half-cell performance, the full cells retain 80 % capacity normalized to the first cycle at 320 mA g^{-1} for only 10 cycles less with 98.5 % average CE. In follow up experiments, the irreversible capacity loss of the full cell is isolated into three components: the NMC811, Si Composite, and mixed electrolyte. Of the three components, the ionic liquid continuously decomposes to form SEI during lithiation of the Si Composite electrode. This mechanism overwhelmingly contributes to irreversible capacity loss in the full cell as evidenced by the retention of full cell with control electrolyte. Further analysis shows that the full cell capacity loss plateaus at the graphite capacity contribution in full cells, thereby indicating that after the Si has been deemed inactive by thick resistive SEI, graphite is the only electroactive material in full cells with the mixed electrolyte. The capacity retention of the full cells at 80 mA g^{-1} , 160 mA g^{-1} , 320 mA g^{-1} , and 640 mA g^{-1} indicate good electrode and electrolyte conductivity with 75 % capacity retention at 640 mA g^{-1} (Figure 4.1.2 (c)). However, the rate performance of the full cell with mixed electrolyte indicates poor retention at higher rates and irreversible capacity loss as the $\text{PYR}_{13}\text{TFSI}$ is continually reduced during Si lithiation and SEI formation (Figure 4.1.2 (d)).

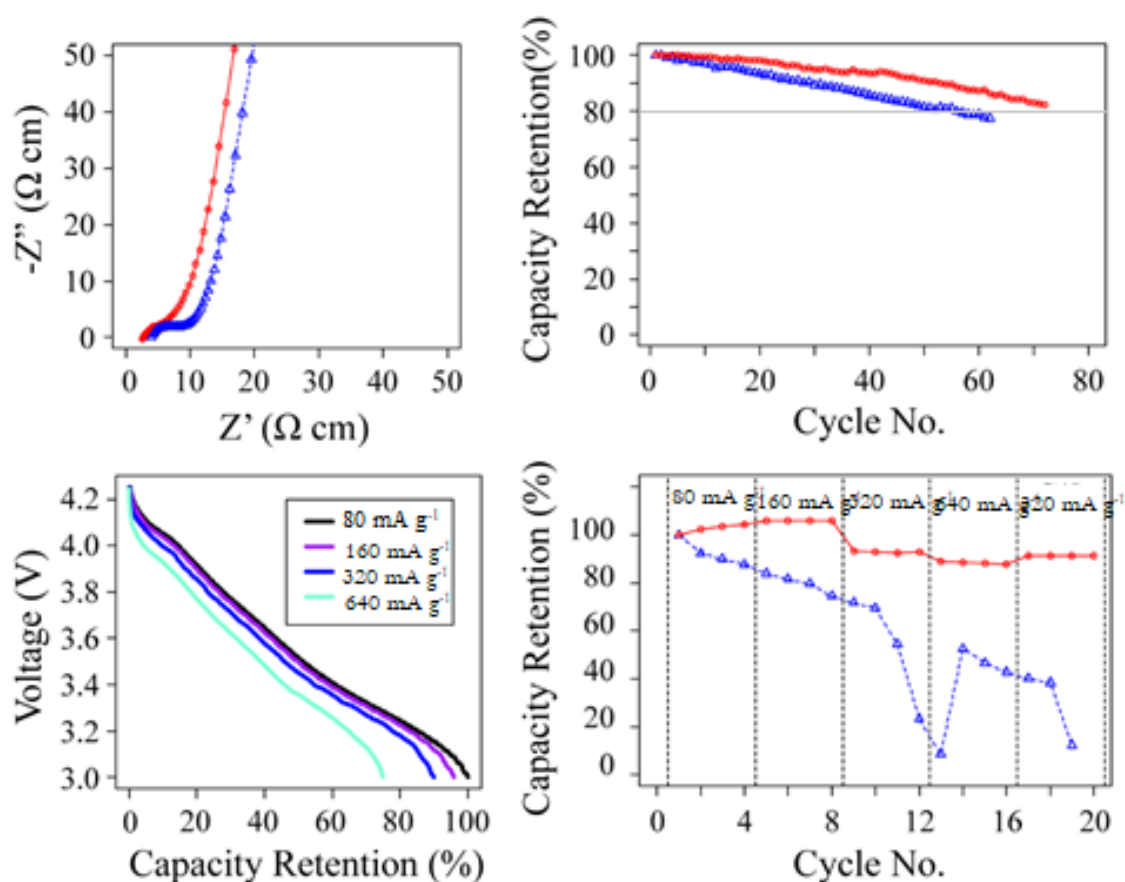


Figure 4.1.2. Electrochemical performance of the functionalized Si Composite electrode matched with 811NMC cathode and mixed ionic liquid electrolyte (blue) or organic control electrolyte (red). (a) Impedance spectra of the full cell configurations in an uncharged state. (b) Capacity retention of the full cells after activation normalized to the first cycle at 320 mA g⁻¹. (c) Capacity retention of the full cell with mixed electrolyte at 80 mA g⁻¹, 160 mA g⁻¹, 320 mA g⁻¹, and 640 mA g⁻¹. (d) The rate performance of the mixed (blue) and control (red) electrolyte. Four cycles between 4.3 V – 3.0 V with a drop-off charge current of 80 mA g⁻¹ were performed at each respective current density.

4.2. Nonflammable Sulfolane Electrolyte

Sulfone-based electrolytes were first synthesized in the late 1990's as a new class of solvent to expand the anodic stability of LIB electrolytes.¹⁴⁰ While conventional carboxylic ester solvents cleave and oxidize between 4.2 and 5.0 V, the first synthesized sulfones (i.e. dimethyl sulfone, DMSF) offer increased stability albeit with high melting points (i.e. 110 °C) due to the high dipole moments and high molecular symmetry. That means that DMSF and similar sulfone are largely unsuitable solvents for ambient temperature electrochemical reactions.¹⁴¹ However, asymmetrical sulfones can have significantly lower melting points by breaking the symmetry, and lowering the lattice energy, of the respective ordered crystalline lattice.¹⁴⁰ Another approach is to use cyclic sulfones with lower reductive stability than open-chain sulfones which are therefore less stable against alkali metals and worse conductors. Sulfones are universally appealing for high voltage cells due to their oxidative stability to at least 5.5 V vs. Li.¹⁴²

Sulfolane (SL), also known as tetramethylene sulfone (TMS), is a cyclic sulfone with high viscosity, poor wettability, and poor inherent compatibility with graphitic electrodes. However, like other sulfones, the high oxidation state of the central sulfur atom (S^{6+}) is different from most carbonate solvents and allows better electronic polarization of the bound oxygen groups. Thus, SL is stable up to high potentials because of its oxygen electron density but also easily reduced by alkali metals. As a result, previous work often focuses on implementing high voltage spinel cathodes with Gr or LTO anodes.^{143–146} Unlike other sulfones, SL benefits from its low melting point (27 °C) which makes it suitable for room temperature systems. The stable interphase formation on graphitic electrodes can be achieved using a lithium bis(fluorosulfonyl)imide (LiFSI) salt. The viscosity of sulfolane has been similarly improved by the addition of various diluents

such as non-solvating fluorinated ethers, such as 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) or bis(2,2,2-trifluoroethyl) ether (BTFE).^{146,147}

In this study, a pure sulfolane system is investigated for layered 532NMC||Gr full cells. Wetting of the electrodes in coin cells is improved by thermally activating the cells at 60 °C for 1 – 2 hours before cycling. For two systems of varying concentration in Figure 4.2.1, the impact of the wetting procedure is significant. More specifically, SL systems tested by EIS before thermal activation have 43 and 503 $\Omega \text{ cm}^2$ with the 3.0 and 3.5 m LiFSI concentrations, respectively. However, after 1 and 2 hours of activation at 60 °C, the impedance of the electrolyte drops to 14 and 18 $\Omega \text{ cm}^2$, respectively. The charge transfer resistance also drops from 87 $\Omega \text{ cm}^2$ to 10 $\Omega \text{ cm}^2$ for the 3.0 m system and 304 $\Omega \text{ cm}^2$ down to around 13 $\Omega \text{ cm}^2$ for the 3.5 m system.

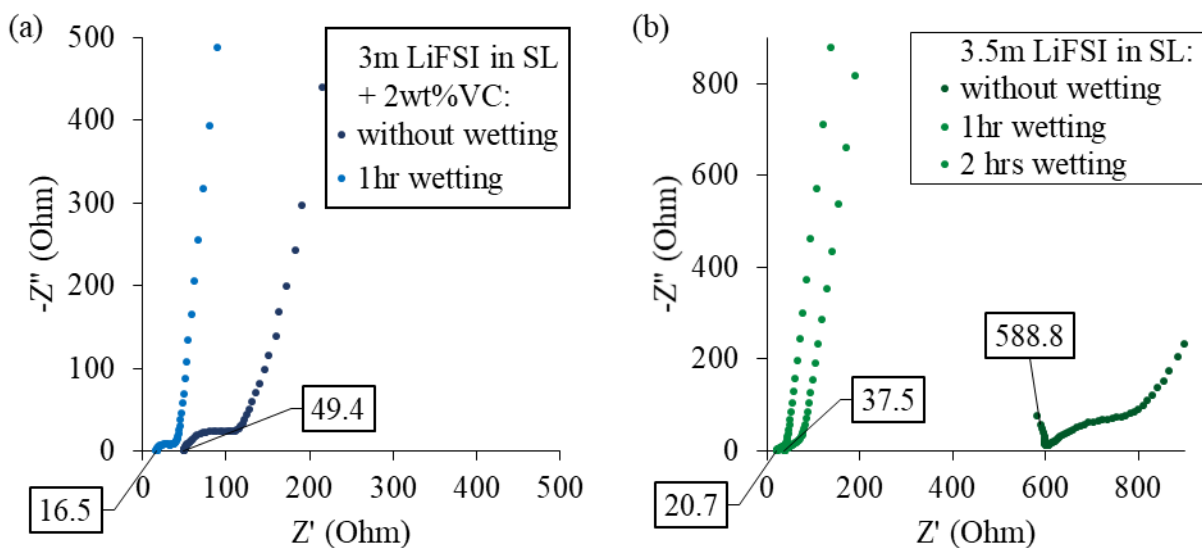


Figure 4.2.1. (a) Impedance spectra of low concentration solution (3.0 m LiFSI) sulfolane electrolyte with 2 wt% VC polymeric additive for SEI formation before (dark blue) and after (cerulean) 1 hour of electrode wetting at 60 °C. (b) Impedance spectra of a high concentration (3.5 m LiFSI) sulfolane electrolyte before (dark green), after 1 hour (forest green), and after 2 hours (neon green) of electrode wetting at 60 °C.

High salt concentration electrolytes are appealing particularly for Si-based systems because of the large Li reservoirs available to compensate for interphase formation and Li depletion.^{143,146} This can be beneficial for cycling but results in more weight and additional cost compared to conventional 1 M systems. As a result, the 3 m LiFSI in SL system is appealing for NMC||Si composite full cells but requires additional optimization for initial SEI formation. Previous reports have demonstrated some anion oxidative instability of FSI with layered LMO-type cathodes over 4.2 V. At a rate of C/25 up to a UCV of 4.3, this results in hours above the anodic limit of the FSI anion. As a result, slow SEI formation rates are avoided in full cell activation protocols. However, this contrasts with the SEI formation requirements for Gr which activates better with slow intercalation of Li⁺ for the different lithiation stages. As a results a thin polymeric SEI former, VC, is implemented to help form a stable graphite SEI at C/2 rates.

A low salt concentration system (2.0 m) is also tested due to its lower viscosity and therefore better conductivity and wetting than the 3.0 m system. Looking at the galvanostatic performance in Figure 4.2.2, both cells achieve close to the theoretical limit for the NMC532||Gr configuration, which justifies the effectiveness of the thermal activation step. Overall, the 3.0 m cell with 2 wt% VC has a higher discharge capacity and a lower coulombic efficiency over 20 cycles. However, neither cell has a CE exceeding 92%. This is reminiscent of the poor CE similar of the ionic liquid and after cycling for 20 cycles with less than 93% CE, this performance eliminated the sulfolane-based system as a nonflammable electrolyte for energy dense full cells. Previous reports have indicated success with mixed sulfolane systems.¹⁴⁴ This is a promising route for future studies of sulfone-based electrolyte.

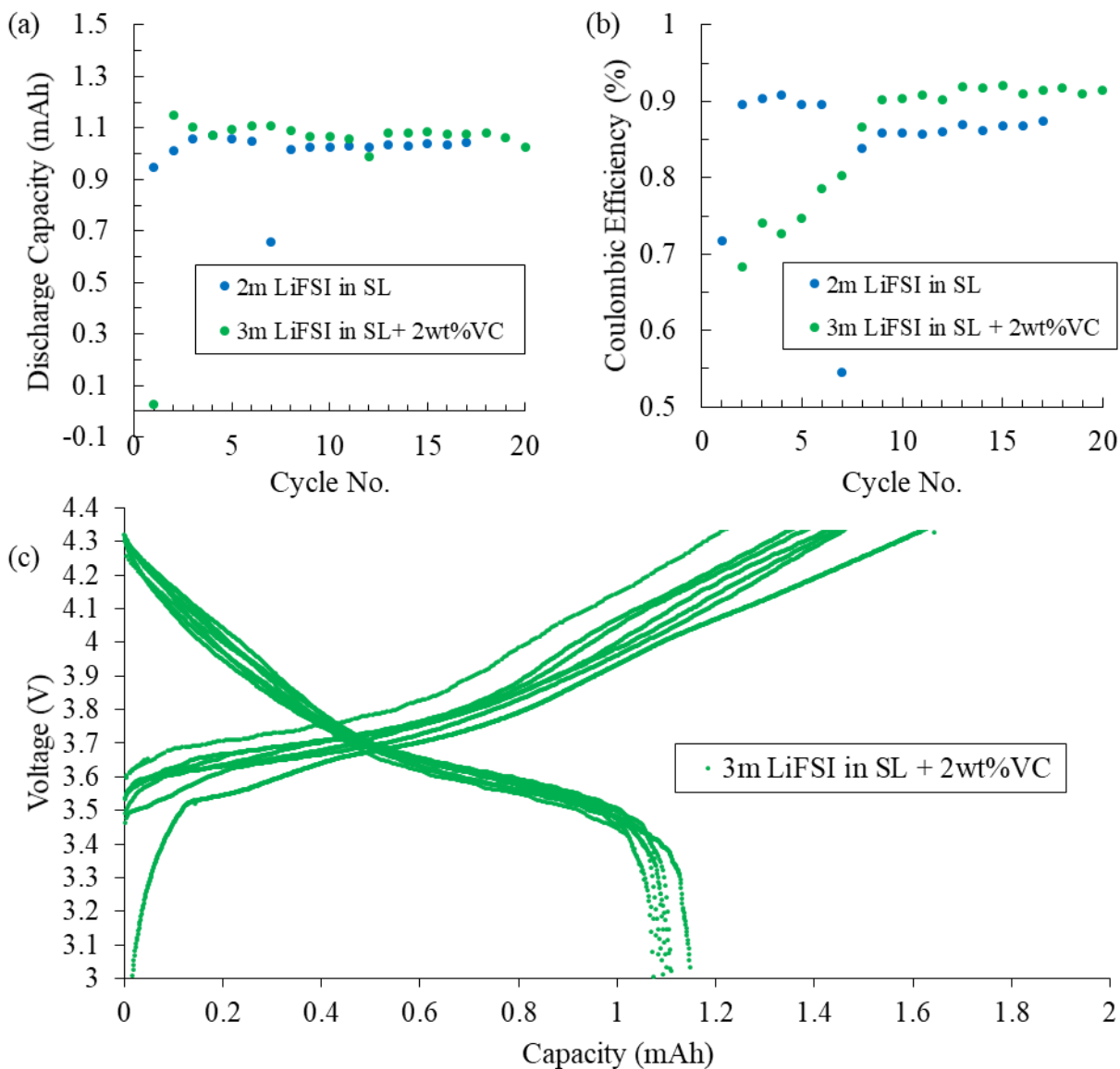


Figure 4.2.2. Full cells with NMC532||Gr electrodes are tested in coin cells with 150 μL of electrolyte deposited on a 150 μm glass fiber separator. (a) Discharge capacity of two sulfolane-based systems with 2m LiFSI (blue) and 3m LiFSI + 2 wt% VC (green). (b) Coulombic efficiency of the two sulfolane-based systems with 2m LiFSI (blue) and 3m LiFSI + 2 wt% VC (green). (c) Capacity versus voltage plot of the 3m LiFSI + 2 wt% VC (green) during CCCV cycling between 4.3 – 3.0 V.

4.3. Flame Retardant Fluorinated Electrolyte

Fluorinated solvents have been investigated since the early 2000's to great success as additives and flame retardant co-solvents in LIBs.^{148–150} In particular, fluorinated ethers (fluoroethers) have been studied as more electrochemically and thermally safe alternatives to the flammable hydrocarbons currently used in commercial cells. However, flammability can be difficult to quantify with liquid electrolytes. Electrolytes that are not completely inflammable provide varying degrees of benefit and safety in LIBs. Previously, Xu *et al.* conducted a modified UL 94 HB test using an inert ball of glass fiber as a reservoir to ascertain the flammability of various solutions.¹⁵¹ After soaking the glass fiber, it was ignited by an open flame and the self-extinguishing time (SET) was recorded. Three categories are defined by this work: (i) SET < 6 s/g is nonflammable, (ii) SET > 20 s/g is flammable with the linear carbonates burnt away, and (iii) SET in between 6 – 20 s/g is flame retardant.

Following this methodology, two fluorinated-based systems, 1 m LiPF₆ in HFE:FEC:FEMC and HFE:FEC:DMC (2:2:6), are tested as well as the MIL electrolyte from Section 4.1 and a baseline organic electrolyte system. Using similar testing protocol and under an open flame, both fluorinated-based systems have SETs < 6 s/g, compared to > 20 s/g for both the mixed ionic liquid and baseline organic electrolyte systems. These results indicate that the fluoroether component, 1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethyl) ether (HFE), can serve as a successful co-solvent to impart strong flame retardant properties on electrolyte systems for energy dense LIBs. Additional videos and documentation of the tests are in the supplementary information. After ascertaining the non-flammability of the fluorinated systems, they were tested more rigorously by various electrochemical methods.

The introduction of fluorine atoms into organic compounds induces a large dipole moment which is expressed as a strong electron-withdrawing inductive effect on the molecule. Positive charge is distributed to the ester backbone and limits electron-releasing behavior. This beneficially reduces the highest occupied and lowest unoccupied molecular orbital (HOMO & LUMO) energies of fluorinated compounds.^{149,152} Which generally results in higher oxidative stability of fluorine-based compounds, such as for F-EPE with a HOMO of -0.35426 au, compared to its non-fluorinated parent compound EPE, with a HOMO of -0.26153 au.¹⁵³ Moreover, 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (F-EPE, industrially known as HFE 458)¹⁵⁴ is a particularly unique solvent which acts as more of a diluent than solvent in Li-ion electrolyte systems due to the high density of electron-withdrawing fluorine atoms. As a result, not only is the oxidative stability of HFE high relative to other organic solvents, but it is not found to significantly solvate the Li cation in LIB electrolytes.

The lowering of the LUMO by fluorine addition contributes some disadvantages for LIB applications. In the case of HFE, a lower LUMO results in some reduction at potentials above the fermi energy of conventional anode materials (C, Si, or Li). This effect is also present in conventional electrolyte solvents and warrants SEI formation on the negative electrode surface. However, with a lower LUMO value, fluorinated solvents are theoretically inclined to react before their non-fluorinated counterparts. For HFE, this behavior is mediated by the poor solvation of LiPF₆ salt, however some reduction of HFE on the negative electrode is to be expected.¹⁵² Due to the large number of fluorine groups, this reduction likely results in LiF formation, but this outcome has not been thoroughly resolved in this study and no mechanism has been proposed in the literature. The synthesis of HFE can be found in the literature¹⁵⁵ and after purifying by fractional distillation and drying over a 4 Å molecular sieve to < 15 ppm H₂O, this solvent can be used in

LIB systems. The fluorinated solvents used in these studies were gratis from Dr. Kang Xu's group at the Army Research Lab.

The first fluorinated system to be electrochemically characterized was 1 m LiPF₆ in HFE:FEC:FEMC with Si composite electrodes from Section 3.3 against Li metal in half cell configurations. The half cells were activated after four CCCV cycles between 0.005 – 1.0 V at 90 mA g⁻¹. Cells were held at 0.005 V for up to 10 minutes or until the current dropped below 90 mA g⁻¹. Then, while maintaining the CV protocol, the half cells are cycled at 180 mA g⁻¹ for 4 cycles before cycling at 320 mA g⁻¹ to test the long-term retention of the half cell. The UMD Si composite electrode (SiGr) has 99.87 and 98.31% average retention per cycle after 55 and 32 cycles, respectively. Showing a significant increase in the retention of the half cell. The electrode performs similarly in the fluorinated electrolyte compared to the baseline organic electrolyte with 10 wt% FEC and 1 wt% VC. The fluorinated cell achieves 89.3% ICE with a first cycle delithiation capacity of 1333 mAh g⁻¹ as seen in Figure 4.3.1 (a). After 60 cycles the capacity has dropped to 855 mAh g⁻¹ while for the organic cell, the capacity has dropped to 956 mAh g⁻¹ from 1394 mAh g⁻¹ with an ICE of 91.3%. Both electrodes originated from the same batch, except the fluorinate electrode was kept in storage under argon for four months. The coulombic efficiency of the fluorinated electrode indicates some form of polarization or side reactions in the fluorinated cell which are further destabilized due to interruption of the cell in the 34th cycle from a power outage. This disruption did not impact the control cell with organic electrolyte which has an average CE of 99.7% after 100 cycles at 320 mA g⁻¹. Although the Si composite undoubtedly performs better in the organic electrolyte, the performance of the half cell with fluorinated electrolyte is comparable, particularly before the electrical disruption. Therefore, the fluorinated electrolyte is suitable for implementation in full cells.

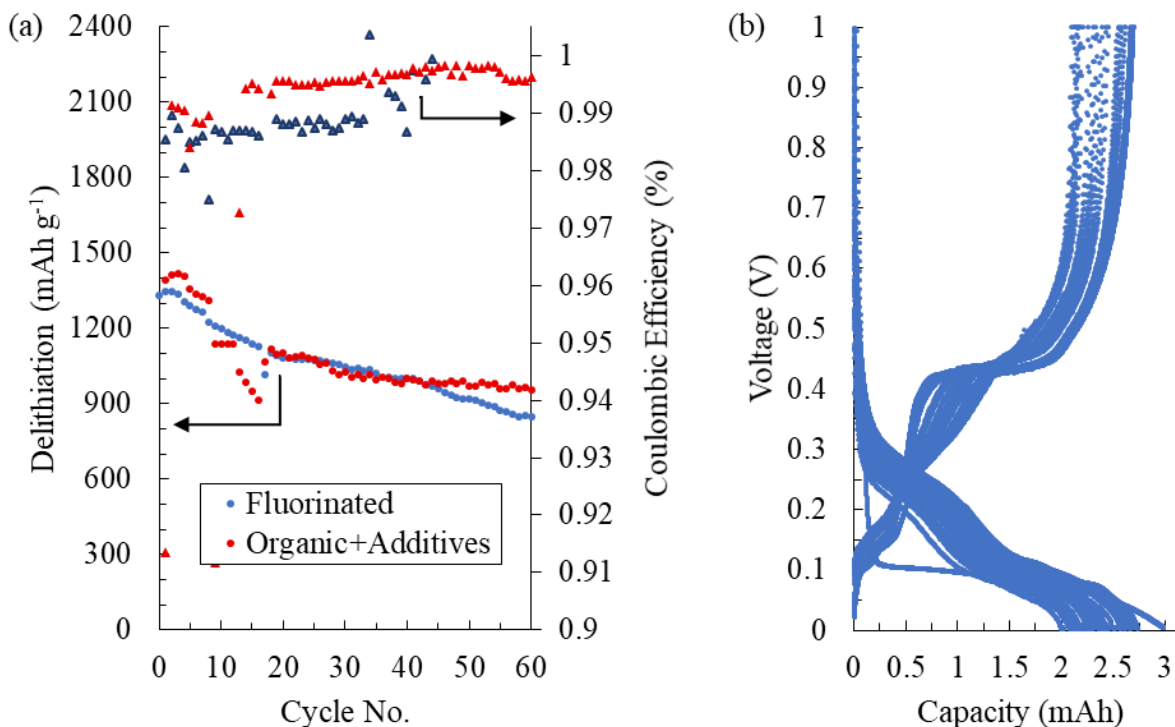


Figure 4.3.1. Galvanostatic cycling of half cells with Si composite electrodes from section 3.3 against Li metal. (a) Delithiation capacity and coulombic efficiency for cells with the fluorinated system versus baseline organic electrolyte with 10 wt% FEC and 1 wt% VC. (b) Lithiation and delithiation curves of the Si composite half cells in fluorinated electrolyte.

The fluorinated system is tested in coins cells with a NMC811 cathode against Si composite (blue), Li metal (purple), and graphite (red) electrodes. The full cells were activated by four CCCV cycles between 4.4 - 3.0 V at 90 mA g⁻¹ and four cycles at 180 mA g⁻¹. Cells were held at 4.4 V for up to 10 minutes or until the current dropped below 90 mA g⁻¹. Then, while maintaining the CV protocol, the cells are cycled at 320 mA g⁻¹ to test the long-term retention of the full cell. The differences between the cells are transparent from the charge/discharge curves and differential analysis of the NMC811||SiGr cell in Figure 4.3.2. The lower discharge potential of the Si-based full cell is more pronounced next to the full cell curves for graphite and lithium metal cells. In the

NMC811||Li cell, the anodic peak at 4.25 V for the H2 $\rightarrow$ H3 oxygen redox peak is clear, following the discussion in Section 4.1. Similarly, in the differential capacity plot, the SiGr cell shows the same redox peak at 4.1 V, with a -150 mV potential shift. The cathodic peak at 3.35 V in the NMC811||SiGr cell is attributed to the NMC transition back to a hexagonal lattice as well at the delithiation of metastable c-Li₁₅Si₄ to a-Li_xSi. The later transition is a high strain delithiation process for the silicon nanoparticles which is widely associated with trapped Li and particle detachment.^{25,156,157} Previous studies have confirmed the complex lithiation/delithiation process of silicon which is described in detail in Section 1.1.

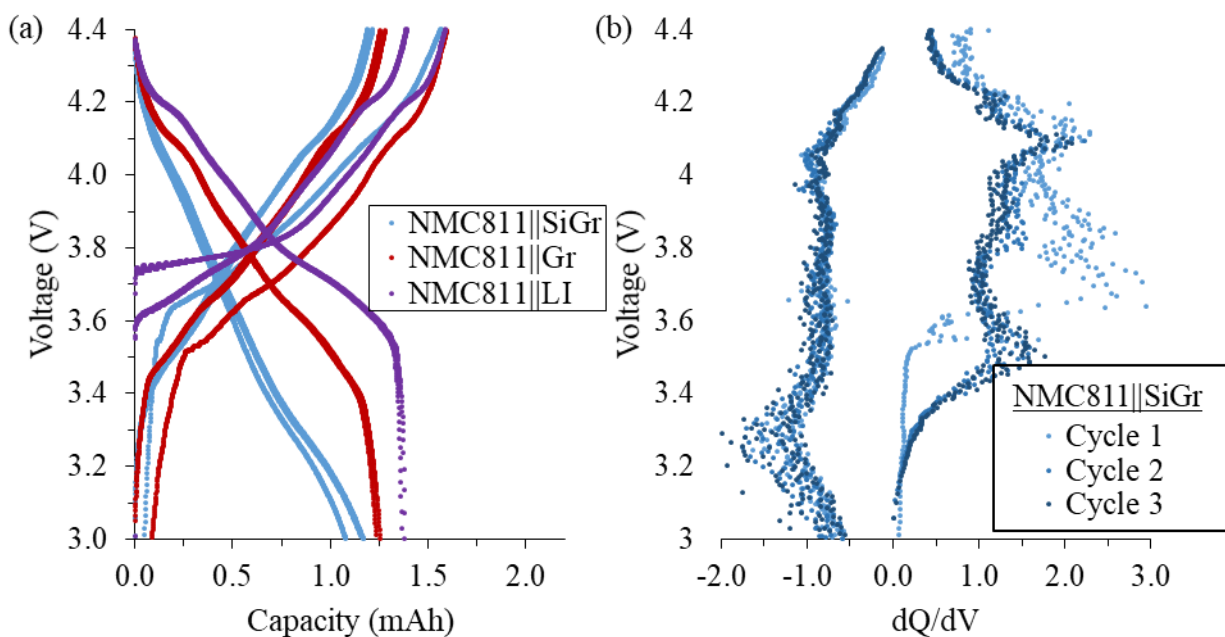


Figure 4.3.2. Galvanostatic cycling of full cells with NMC811 cathodes against Si composite (blue), graphite (red), and lithium metal (purple) electrodes. (a) Charge and discharge curves of the cells in 1 m LiPF₆ in HFE:FEC:FEMC electrolyte (2:2:6 by wt). (b) Differential capacity analysis of the first three cycles of the NMC811||Si composite cell.

The 811NMC||SiGr full cell, using a Si composite electrode described in Section 3.3, achieves 99.39 % average retention per cycle after 100 cycles at C/5. While the 811NMC||Gr full

cell, using a graphite electrode from ANL (A002B), and the 811NMC||Li cell achieve 99.77 % and 99.93 % average retention per cycle under the same timescale, respectively. This results in 59 %, 82 %, and 94 % capacity retention of the SiGr, Gr, and Li full cells, respectively, after 100 cycles at C/5. However, the average coulombic efficiency of the full cells in the same window is 99.2%, 96.8%, and 89.0% for the SiGr, Gr, and Li full cells, respectively.

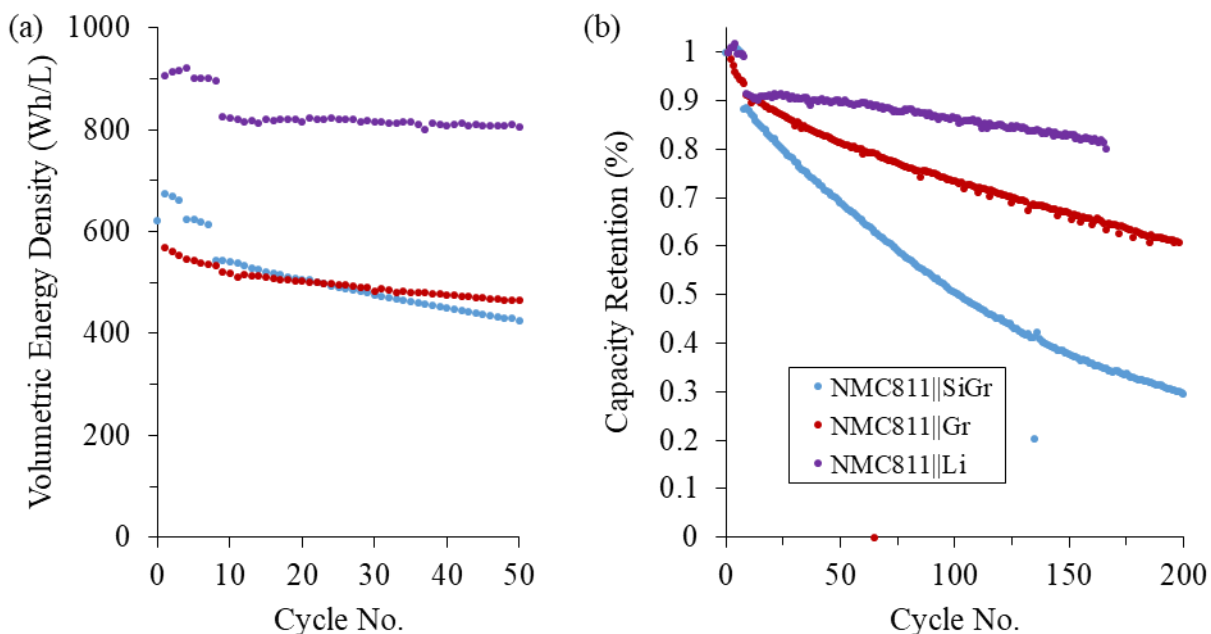


Figure 4.3.3. (a) Volumetric energy density and (b) capacity retention of full cells with NMC811 cathodes against Si composite (blue), graphite (red), and lithium metal (purple) electrodes in 1 m LiPF₆ in HFE:FEC:FEMC electrolyte (2:2:6 by wt).

The initial results of the fully fluorinated system are exceedingly promising for flame retardant and energy dense full cells. However, the fluorinated solvents add significant cost to the battery system which still needs to be evaluated within the context of the electrochemical performance. Breaking down the system into the three solvents, FEC, FEMC, and HFE, the two former solvents immediately stand out as components that may be replaceable. Both fluorinated solvent provide lower LUMO and HOMO values than their non-fluorinated counterparts. This

imparts better oxidative stability but also significantly impacts interphase formation during reduction of the electrodes.

An extensive literature has been amassed on the impact of FEC in various full and half cell systems, which is built on in Section 4.4.^{91,154,158–167} Si-based electrodes, in particular, benefit immensely from the decomposition of FEC for a thinner and more polymeric SEI. Thorough investigations during the multi-laboratory “Silicon Deep Dive” effort have opined about the breathable nature of the silicon SEI which is difficult to characterize and even more difficult to observe.^{168,169} One study by Veith et al. cycled 99.5 nm *a*-Si films against Li foil to examine the SEI formation with and without FEC by *in situ* neutron reflectometry (NR), *ex situ* x-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR).¹⁶⁴ Although the cells are only cycled as a-Li_xSi between 0.1 - 1.5 V in 1.0 M LiPF₆ EC:DMC (3:7 wt%) +/- 5 wt% FEC, the conclusions from this work are well-conceived and have some translation to variations on the pure Si and FEC systems with binder, conductive additives, and graphite. For instance, in Veith’s work, hydrolysis and formation of a condensed 3 nm passivation layer is observed on the native Si oxide at OCV with or without FEC. Then with FEC, the Si SEI breathes in 1.3 nm amplitudes between lithiation and delithiation but without FEC, the same amplitudes are > 6 nm in the opposite direction. This refers to the observed increase in SEI thickness during delithiation without FEC and the decrease in thickness with FEC as seen in Figure 4.3.4. In the text, this result is attributed to FEC-based C-O functionalities on the silicon surface which act as SEI precursor to reform a more polymer SEI during lithiation. This hypothesis is made more compelling by the coupled NR and XPS measurements which indicate the polymeric versus inorganic context of the systems with and without FEC. In the system without FEC, less polymeric and more inorganic species such as LiF upon delithiation can be attributed to increased salt

decomposition. Therefore, the addition of FEC in Si-based systems limits salt decomposition and it is speculated that FEC reduces at 1.1 V vs. Li^+ on the Si surface to act as an SEI precursor as the system breathes with each cycle. This provides a compelling argument for maintaining the FEC content in the fluorinated electrolyte system.

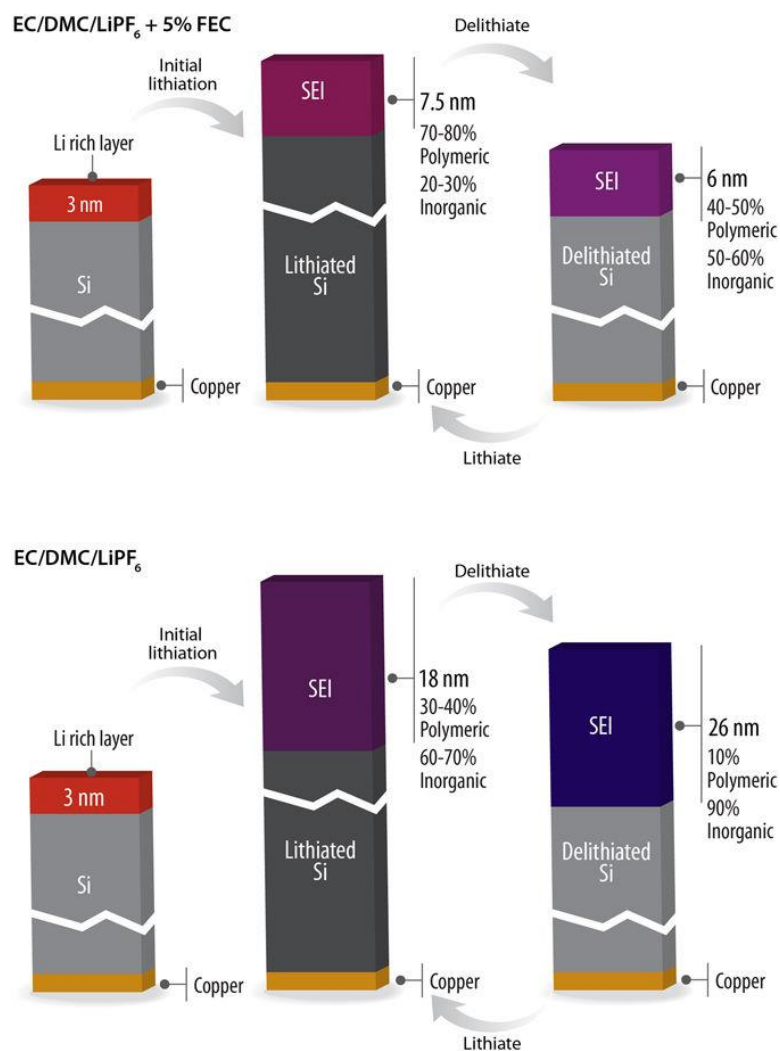
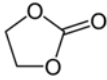
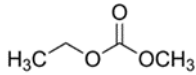


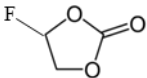
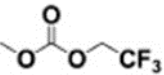
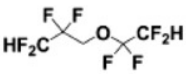
Figure 4.3.4. Graphical illustration of SEI formation with and without FEC as interpreted from *in situ* NR, *ex situ* XPS, and FTIR measurements by Veith *et al.*¹⁶⁴

Next, the FEMC solvent is tested against conventional low viscosity solvents to develop the optimized fluorinated electrolyte system. The FEMC solvent is understood to serve four key functions in the fluorinated system, including: (i) lowering the viscosity of the system and thereby

raising the ionic conductivity to $> 10^{-3}$ S/cm, (ii) potentially contributing to the overall flame retardant properties of the electrolyte, (iii) providing oxidative and thermal stability, and (iv) providing fluorinated species which impact SEI formation and lead to improved electrochemical performance. In terms of the viscosity and ionic conductivity of the system, among the widely accepted linear carbonate solvents, DMC has a low viscosity at 25 °C of 0.748 cP, with a dielectric constant of 2.82 compared to $\eta = 1.4$ cP and $\epsilon_r = 122$ for FEMC. Initial investigations of fluorinated systems with FEMC replaced by DMC also indicate no significant impact on the flammability of the system. The only other conditions potentially negatively impacted by the substitution of FEMC with DMC are (iii) and (iv) as they pertain to the electrochemical performance of energy dense NMC||SiGr full cells. The oxidation potential of fluorinated and non-fluorinated solvents are given in Table 4.3.1 to better denote the changes in electrolyte oxidation and reduction. It is reasonable to expect that the fluorinated linear carbonate, FEMC, would contribute additional LiF during SEI formation on the negative electrode which is known to contribute to more uniform and dense SEI particularly in lithium metal based systems.¹⁷⁰ However, after considering the contributions from Veith *et al*¹⁶⁴ and others,^{171,172} it can be hypothesized that LiF formation is undesirable for breathing Si SEI and, therefore the low LUMO of FEMC could negatively impart a more inorganic SEI on the surface of the Si additive.

Table 4.3.1. Structure, oxidation potential, and HOMO/LUMO energies of cyclic and linear carbonates with and without fluorinated species.^{153,173}

Molecule	Structure	P _{ox} (V theory)	P _{ox} w/Anion Effect	HOMO (au)	LUMO (au)
EC		6.91	6.17 (PF ₆ ⁻)	-0.31005	-0.01067
EMC		6.63 (DMC: 6.71)	(DMC: 6.07)	-0.29905	0.00251

FEC		7.24	6.44 (PF ₆ ⁻)		
F-EMC		7.01	6.26 (PF ₆ ⁻)	-0.31946	-0.00363
HFE		7.24		-0.35426	-0.00356

Further investigation of the electrochemical performance of the FEMC and DMC based fluorinated electrolytes is conducted in full cell configurations using NMC532 positive electrodes and SiGr negative electrodes. The volumetric energy density, discharge capacity, energy retention, and voltage hysteresis of the cells are given in Figure 4.3.5. The two electrolyte systems are tested in duplicate stainless steel coin cells with CCCV protocol between 4.3 and 3.0 V. The electrodes were gratis from ANL's CAMP facility (C015 and A011). In Figure 4.3.5 (b) the initial discharge capacity of the four cells is found to be within a 10 % deviation of one another. However, the retention of the systems quickly deviates as the HFE:FEC:FEMC system reaches 80 % capacity retention within 30 cycles at C/5. In comparison, the HFE:FEC:DMC system retains its capacity for twice as many cycles with a starting energy density of around 600 Wh L⁻¹. The superior performance of the DMC based system is not easily explained by electrochemical characterization. However, the voltage hysteresis of the cells, given in Figure 4.3.5 (d), provides some additional insight into the degradation of the FEMC and DMC based cells. The voltage hysteresis is calculated by the equation below and normalized to the first cycle at C/5, i.e. the 8th cycle.

$$V_{hys} = \frac{\frac{E_8^{dis}}{Q_8^{dis}} - \frac{E_8^{ch}}{Q_8^{ch}}}{\frac{E_n^{dis}}{Q_n^{dis}} - \frac{E_n^{ch}}{Q_n^{ch}}} = \frac{V_{8,avg}^{dis} - V_{8,avg}^{ch}}{V_{n,avg}^{dis} - V_{n,avg}^{ch}} \quad (4.3.1)$$

where E_n^{dis} is the discharge energy of the nth cycle, E_n^{ch} is the charge energy of the nth cycle, Q_n^{dis} is the discharge capacity of the nth cycle, Q_n^{ch} is the charge capacity of the nth cycle. It is evident

from the voltage hysteresis plot that the overpotential of the FEMC based cells is rising significantly faster than that of the DMC based cells. Additionally, the drop in capacity does not follow the same trend as the incremental voltage hysteresis in the cell. While the voltage hysteresis is linear and only reaches 80 % after 100 cycles for the FEMC cells, the energy retention is parabolic and reaches between 50 – 60 % after 100 cycles. This difference between the trends for voltage hysteresis and energy retention can be attributed to loss of capacity without an increase in overpotential. For instance, by the sudden loss of electroactive Si due to detachment or excessive SEI. More importantly, this result indicates improved electrochemical performance by swapping out the fluorinated carbonate, FEMC, for the less viscous and non-fluorinated DMC.

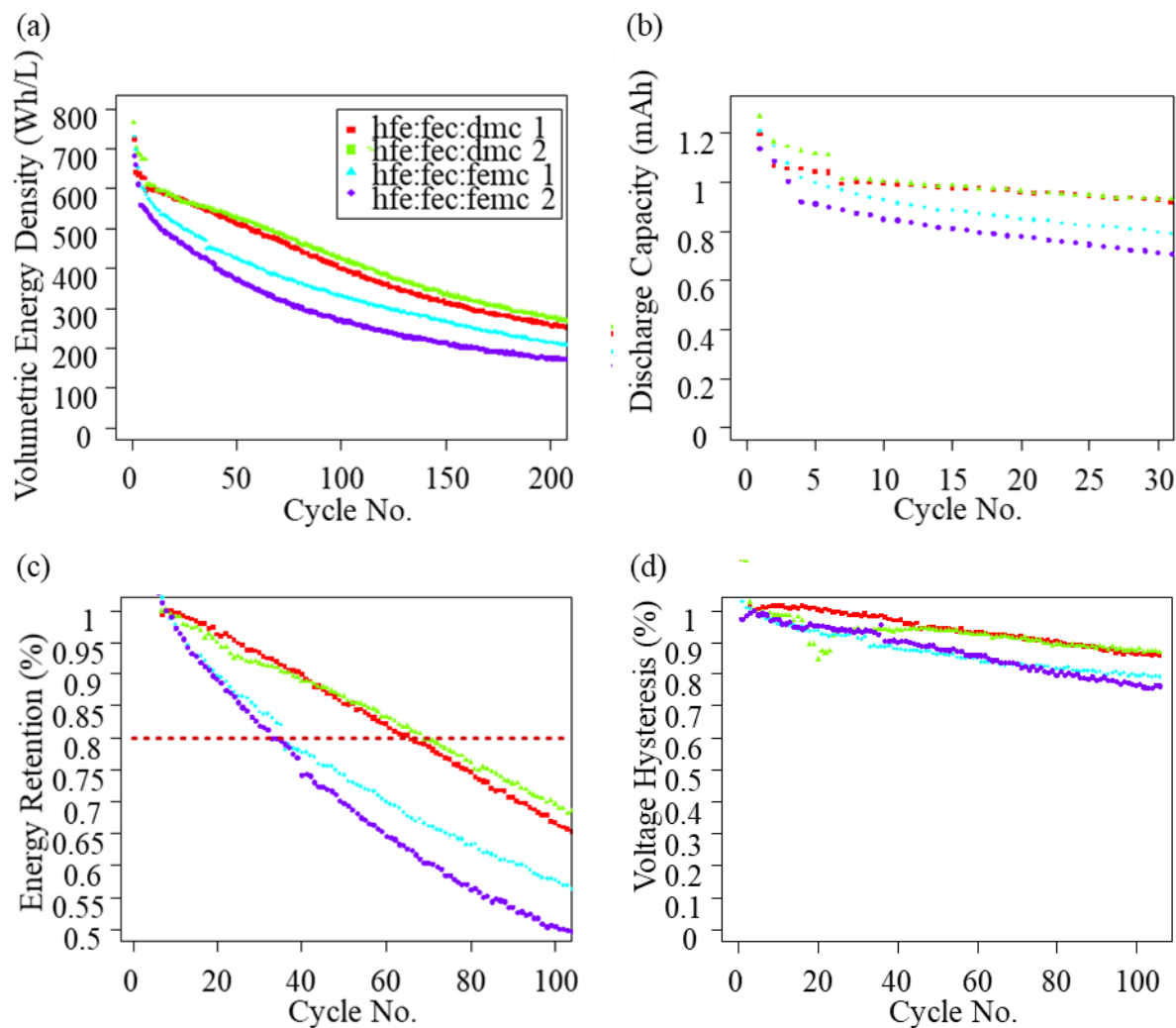


Figure 4.3.5. (a) Volumetric energy density, (b) discharge capacity, (c) energy retention, and voltage hysteresis of duplicate NMC532||SiGr full cells are tested in either 1m LiPF₆ electrolyte with HFE:FEC:DMC (2:2:6 wt%) (red & green) or HFE:FEC:FEMC (2:2:6 wt%) (blue & purple) solvents. The cells are cycled by CCCV protocol in stainless steel coin cells between 4.3 and 3 V.

The oxidative stability of the optimized fluorinated electrolyte with HFE:FEC:DMC solvents in 2:2:6 wt% is tested against conventional EC:EMC electrolyte using 1 m LiPF₆ salt. The linear sweep voltammetry (LSV) curves of both systems are included in Figure 4.3.6 with the control system in blue and the fluorinated in green. The electrolyte is tested in stainless steel coin

cells with aluminum-coated top caps and 250 μm glass fiber membranes. Li metal pellets were placed on Cu foil and stainless steel electrodes on the bottom cap. The top cap was used without further preparation. The LSV curves indicate oxidation in the EC:EMC cell starting at 3.5 V and modestly rising to 1 μA at 4.24 V. In comparison, the fluorinated HFE:FEC:DMC cell shows some oxidation at 4.04 V which rises to 1 μA at 4.51 V. Considering the lack of additional additives and co-solvents, the fluorinated system shows high oxidative stability for high voltage and energy dense full cells. This performance presents an appealing platform for cycling high voltage NMC||SiGr cells.

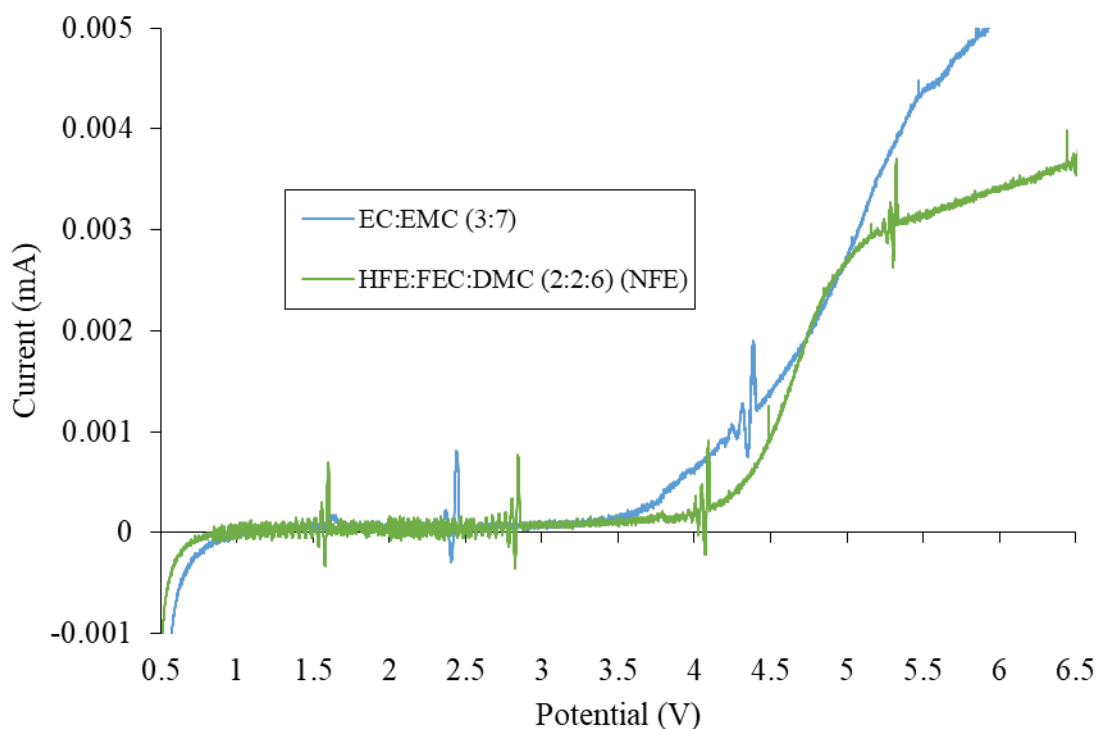


Figure 4.3.6. Linear sweep voltammetry of a conventional electrolyte system with 3:7 wt% of EC:EMC solvents versus HFE:FEC:DMC solvents with 2:2:6 wt%.

Next, variations on the original and optimized fluorinated system are tested in NMC532 half cells. The purpose of this experiment is to define the impact of the fluorinated cyclic carbonate

(FEC:DMC vs. EC:EMC), fluorinated linear carbonate (HFE:FEC:FEMC vs. HFE:FEC:DMC), and fluorinated ether (HFE:FEC:DMC vs. FEC:DMC) against non-fluorinated counterparts in cells with NMC532 cathodes and Li metal anodes. Previous reports, including work by Fan *et al.*,¹⁷⁴ show significant improvement in high voltage cathodes against Li metal anodes with the all fluorinated system with HFE:FEC:FEMC solvents. In this study, the authors report suppressed dendrite formation and high coulombic efficiencies of 99.93 % in NMC811||Li configurations. This improvement is attributed, in this work and others,⁹² to the formation of a 5 – 10 nm thick, highly fluorinated interphase on the Li metal anode which inhibits electrolyte oxidation and transition metal dissolution. These results run contrary to the NMC532||SiGr full cells tested in Figure 4.3.5 which show worse retention and overall performance of the fully fluorinated electrolyte system with FEMC solvent compared to the same system with the non-fluorinated linear carbonate DMC, instead. The results in Figure 4.3.5 suggest that the decomposition of FEMC into additional LiF on the Si surface is undesirable compared to the decomposition of FEC, which is responsible for a more polymeric SEI closer to the Si surface and radical polymerization of on the Si surface. Therefore, one of the most optimal systems for Li metal anodes, the fully fluorinated system, would be less ideal than the same system which prioritizes a polymeric, FEC-derived SEI due to the high LUMO of a non-fluorinated linear carbonate rather than higher fluorine content and additional LiF from an SEI derived from fluorinated cyclic and linear carbonates.

The performance of NMC||Li cells in various electrolyte systems is depicted in Figure 4.3.7. From this figure, the results of Fan *et al.* are confirmed and the cells with the fully fluorinated electrolyte (HFE:FEC:FEMC) perform the best with the NMC positive electrode and Li metal anode. The average CE of the four systems are 99.72, 99.67, 99.59, and 99.38 % for the HFE:FEC:FEMC, HFE:FEC:DMC, FEC:DMC, and EC:EMC cell, respectively. The higher

coulombic efficiency of the FEMC system indicates a better SEI is formed during the repeated stripping and plating on the Li metal anode. This is the opposite result from the cells with SiGr electrodes in Figure 4.3.5. The improvement in performance with the fluorinated ether is best realized by comparing the HFE:FEC:DMC and FEC:DMC cells. The later shows significantly worse energy retention than the cells with a fluorinated ether. This can be attributed to the high oxidative stability of the electrolyte with the HFE, fluorinated ether. After 100 cycles at C/5, the cell with the fluorinated ether (HFE:FEC:DMC) retains 70.9 % of its initial energy or 606 Wh L⁻¹ compared to 70.2 % and 592 Wh L⁻¹ for the FEC:DMC system, and 73.7 % and 625 Wh L⁻¹ for the HFE:FEC:FEMC system. And the last parameter to be analyzed in this experiment, the fluorination of the cyclic carbonate, is considered by comparing the FEC:DMC and EC:EMC cells. The presence of the fluorinated FEC in the electrolyte system greatly improves the performance of the NMC532||Li cells relative to the EC:EMC system as evidenced by the energy retention. The FEC:DMC system retain 70.2 % of its initial energy at C/5 after 100 cycles while the EC:EMC system only retains 66.9 % of its energy. This represents a dramatic jump in performance and is further supported by the higher coulombic efficiency of cells with additional fluorinated species. From these results, it is clear that, unlike with the SiGr cells, the best electrolyte for full cells with Li metal anodes is fully fluorinated.

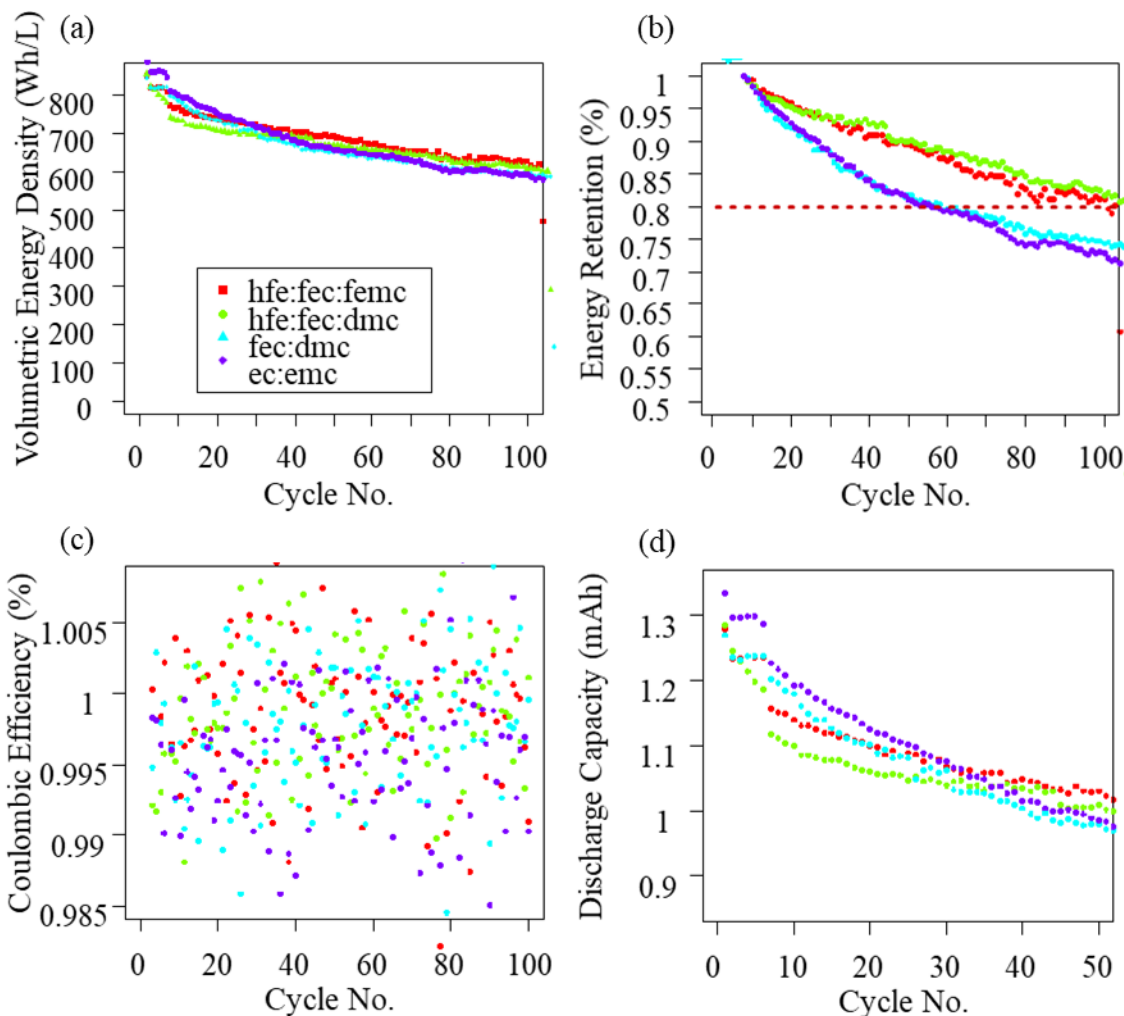


Figure 4.3.7. (a) Volumetric energy density, (b) energy retention, (c) coulombic efficiency, and discharge capacity of NMC532 half cells in four different 1m LiPF₆ electrolyte systems, including HFE:FEC:FEMC (2:2:6 by wt) (red), HFE:FEC:DMC (2:2:6 by wt) (green), FEC:DMC (1:4 by wt) (blue), and EC:EMC (3:7 by wt) (purple). Cycled by CCCV protocol in stainless steel coin cells between 4.3 and 3 V.

The last parameter investigated with the fluorinated system optimized for SiGr cells, i.e., HFE:FEC:DMC, is the stoichiometry of the NMC cathode in full cells with SiGr negative electrodes. Conventionally, high nickel-content cathodes provide reduced stability in full cells due

to surface oxygen redox reactions and unstable phase formation during delithiated up to 80 – 90 % state of charge, as explained in Section 4.1.^{135,175–177} However, the use of a SiGr negative electrode could lead to unexpected deviations in performance as observed for the fully fluorinated HFE:FEC:FEMC electrolyte versus the more optimum HFE:FEC:DMC system. Furthermore, previous work on SiGr full cells has indicated improved performance with the addition of lithium oxalate and carbon dioxide additives, the latter of which is a by-product of radical oxygen redox in high-Ni content cathodes.^{20,178,179} Therefore, NMC positive electrodes with 811, 622, and 532 stoichiometry are tested against SiGr negative electrodes with the results plotted in Figure 4.3.8 and the key performance metrics are given in Table 4.3.2.

Table 4.3.2. Performance metrics of the NMC811, NMC622, and NMC532 cells with SiGr negative electrodes in 1 m LiPF₆ in HFE:FEC:DMC electrolyte

Metric	811-1	811-2	622-1	532-1	532-2
Initial E ₁ (Wh)	5.80	5.85	4.20	4.25	4.49
ICE (%)	0.792	0.784	0.777	0.680	0.768
E ₁₀₀ (Wh)	2.66	2.67	2.32	2.35	2.50
Avg. CE @ C/5 (%)	0.995	0.995	0.992	0.951	0.992
Avg. Retained @ C/5 (%)	0.995	0.995	0.995	0.996	0.996
Avg. Retained in 30 cycles @ C/5	0.995	0.993	0.994	0.997	0.997
% E lost in 30 cycles	-0.135	-0.175	-0.134	-0.094	-0.102
% E lost in 100 cycles	-0.541	-0.544	-0.448	-0.447	-0.443

The initial energy and discharge capacity of the cells varies with the mass loading and theoretical capacity of the electrodes, however each cell is cycled between 4.35 – 3.0 V by CCCV protocol in stainless steel coin cells. The NMC811 electrodes have slightly higher initial capacity, ICE, and energy but eventually suffer the greatest percent of the energy lost after 30 and 100 cycles. The average coulombic efficiency of NMC811||SiGr 1 is 99.50% after 100 cycles while the NMC811||SiGr 2 is 99.49%. In comparison, the NMC532 cells have low average coulombic

efficiencies, 99.19% after 100 cycles, but the best retention and the least voltage hysteresis as indicated in Figure 4.3.8 (c). In general each plot follows a similar trend with the 811 stoichiometry showing the least stability with the highest initial output, followed by the 622 stoichiometry and then the 532 stoichiometry, which is the most stable with the lowest initial output. These results do not deviate significantly from conventional systems with pure Gr-based electrodes. As a result, the NMC532||SiGr configuration will be used in the subsequent section.

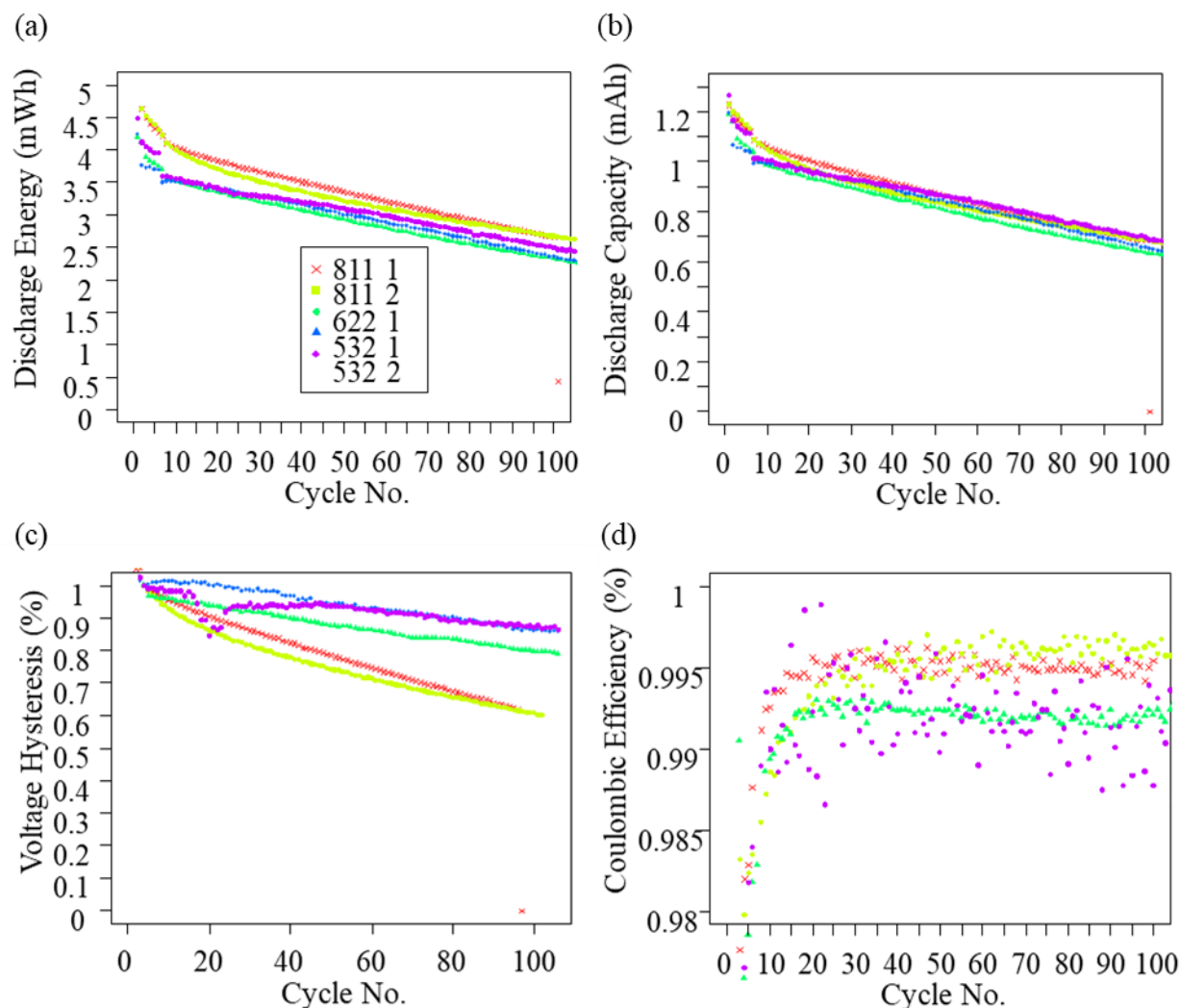


Figure 4.3.8. (a) Volumetric energy density and (b) capacity retention of full cells with NMC811 (red and yellow), NMC622 (green), and NMC532 (blue and purple) positive electrodes against Si

composite electrodes in 1 m LiPF₆ in HFE:FEC:DMC electrolyte (2:2:6 by wt). Cycled by CCCV protocol in stainless steel coin cells between 4.35 and 3 V.

4.4. Additives for Silicon-based Full Cells

An ideal solid electrolyte interphase (SEI) provides a hermetic seal around electronically conductive surfaces, shielding electrolyte from further reduction and oxidation. However, in high volume expansion electrodes, such as Si composites, this seal is easily broken, which leads to a series of compounding issues, including, but not limited to: rising impedance, thicker SEI, voltage hysteresis, and electrolyte consumption. Practically every battery material and environmental parameter plays into the formation of SEI, but the optimization of low-weight percent additives is one of the most direct methods for engineering interfacial properties. Consequently, after optimizing the negative electrolyte, electrolyte system, and positive electrode, a number of experiments were performed to investigate additives for the NMC532 || 1 m LiPF₆ in HFE:FEC:DMC || SiGr system. But first, additives were screened and considered in a thorough literature review, before procuring and proceeding with a sequence of electrochemical tests. The list of additives down-selected from the initial literature review are given below in Table 4.4.1, with the acronym, corresponding author, and a brief discussion of the interfacial impact.

Table 4.4.1. List of pertinent additives for NMC||Si full cell configurations found in the literature.

Additive Name	Acronym	PI	Purpose
Fluoroethylene carbonate	FEC	Dahn	Negative electrode additive. Forms a more polymeric SEI and provides a F-group
Vinylene carbonate	VC	(Asahi?) ¹⁸⁰	Negative electrode additive. Forms a more polymeric SEI
Lithium nitrate	LiNO ₃	DOE ¹⁸¹	Dual-electrode additive. SEI film forming additive particularly for Li metal
Lithium bis(fluorosulfonyl) amide	LiFSI	Wentao Li (BASF) ¹⁸²	Dual-electrode additive. High conductivity, thus providing better rate and low temperature performance

diethyl pyrocarbonate	DEPC	Chevrier ²⁰	Negative electrode additive. Forms CO ₂ and EtOH from H ₂ O.
ethylene sulfate	DTD	Dahn ¹⁸³	Positive electrode additive. Low ΔV.
Lithium oxalyl-difluoroborate	LiDFOB	Sheng Shui Zhang	Dual-electrode additive. Thicker anode and cathode SEI.
tris(trimethylsilyl) phosphite	TTSPi/TMSPi	Abraham ¹⁸⁴	Positive electrode additive developed by Wildcat. Hinders LiPF ₆ decomposition, scavenged HF, therefore limited Mn/Ni dissolution and forms cathode SEI
1,3-propanediolcyclic sulfate	PCS	Guanglei Cui ¹⁸⁵	Negative electrode additive. Lower LUMO than EC, therefore less EC reduction or less C ₂ H ₄ generation.
prop-1-ene, 1-3 sultone	PES	Dahn ¹⁸⁶	Negative electrode additive. SEI film forming additive, eliminates gas production
methylene methanedisulfonate	MMDS	Dahn ¹⁸⁷	Positive electrode additive. Modification of CEI, lower impedance and gas production
lithium fluoromalonato (difluoro)borate	LiFMDFB	Nam-Soon Choi ¹⁸⁸	Dual-electrode additive. Lower LUMO and higher HOMO than EC and FEC. Reacts with CO ₂ and O ₂ gas.
triphenylphosphine oxide	TPPO	Tobias Placke ¹⁸⁹	Positive electrode additive. Low LUMO so TPPO reduces prior to electrolyte solvent molecules.
2,4,6 trivinylcyclo triboroxane	tVCBO	Abraham ¹⁹⁰	Negative electrode additive. Helps polymerization
lithium difluorophosphate	LiPO ₂ F ₂	Dahn ¹⁹¹	Reduces impedance growth and gassing but does not work with PES211, only FEC and DTD when tested.
methyl acetate	MA	Dahn ¹⁹²	Increases conductivity, rate and low T performance by lowering viscosity. Slightly reduces cyclability
lithium oxalate	Li ₂ C ₂ O ₄	Gasteiger ¹⁷⁹	Dual-electrode additive. oxidizes to CO ₂ and acts as an H ₂ O/H ⁺ scavenger yielding lithium formate and LiCO ₃ .

A list of the additives tested in subsequent experiments, characterizations performed, and the condensed results are in Table 4.4.2. The tests include CCCV galvanostatic cycling in the system-of-interest, electrochemical impedance spectroscopy, linear sweep voltammetry between a Li counter electrode and an Al-clad top cap, voltage drop tests, and impedance tests. Cells generally used electrolyte including the flame retardant fluorinated ether and LiPF₆ salt from section 4.3, but additional experiments with EC:EMC solvents were also conducted. The chief

purpose of the additives and salts in this work is to optimize the SEI on the electrodes such that (i) interphase layers are altered to be dense and more polymeric, (ii) metal dissolution is inhibited, (iii) cathode outgassing is reduced although outgassing in select scenarios might be beneficial,⁴⁶ or (iv) contaminants such as HF acid are curtailed. A design of experiments approach is applied to test the various systems and compositions with at least one duplicate cell for each trial.

Promising additive systems are meticulously reexamined, particularly after adjustments to the electrode design or composition. Additional emphasis is placed on confirming the safety of the electrolyte system as well as the stability against silicon, carbon, and nickel oxide-based electroactive materials for high coulombic efficiencies. Cells are initially activated at C/20 before cycling at C/5. Many of the additives and electrolytes were provided by the Army Research Lab while Si composite negative electrodes (A011), graphite electrode (A002b), and various NMC electrodes (C013, C015, C018, C019) graciously provided by Argonne's Cell Analysis, Modeling, and Prototyping (CAMP) facility.

Table 4.4.2. List of the tests conducted for various additives and a brief conclusion of the results.

Additive Name	Tests Conducted					Results
	CCCV	EIS	LSV	V-drop	Imp.	
FEC	X	X	X	X	X	Maintained
VC	X	X				Abandoned
DEPC	X	X				Suspended
LiNO ₃	X	X				Suspended
DTD	X					Abandoned
LiFSI	X	X	X	X		Suspended
TTMSPi	X	X	X	X		Abandoned
LiDFOB	X	X	X	X	X	Maintained

The baseline additive package adopted at the start of this work consisted of 10 wt% fluorethylene carbonate (FEC) and 1 wt% vinylene carbonate (VC). A thorough library exists on both additives for full cells with Si electrodes. While VC is widely successful as an additive in

alkyl carbonate systems to form a more polymeric SEI, its voltage stability above 4.1 V and its usefulness with Si electrodes is less ensured than FEC.^{193,194} FEC is easily the most studied additive for Si containing systems with enough content to write an extensive history on the subject with conflicting conclusions for every scenario.^{36,45,89,91,91,100,104,112,113,115,116,154,161,164,166,168–170,185,195–208} A number of key properties of FEC-derived SEI formation on Si can be carefully extracted from these works. However, it is crucial to consider the context and experimental conditions of each study. For instance, sum frequency generation (SFG) vibrational spectroscopy indicates that FEC-induced monolayers of aligned, up-right solvent species specifically adsorb with their carbonyl (C=O) and oxygen atom against Si surfaces. As a result, additional solvent layers are packed on top of the monolayer in a perpendicular orientation with surface-parallel alignment.^{166,200} However, this result was using an e-beam deposited, binder-free, α -Si thin film. Results for thin film versus nanoparticles versus silicon with varying degrees of crystallinity and oxide content all have a significant impact on the resultant SEI. The work in Chapter 3 pertains most to Si composites with crystalline nanoparticles wrapped or coated in carbon with PAA:SBR binder. While certain works by Gasteiger and 3M group in St. Paul, Minnesota overlap well with this design, few other fundamental studies on FEC-derived SEI formation do.

It has also been well established that SEI formed with FEC tends to be thinner and more compact on almost any Si surface.^{91,113,116,164,206,207} Looking at the chemical signature from ⁶Li NMR, neutron reflectometry, and X-ray photoelectron spectroscopy (XPS) of the FEC-derived SEI gives a sense for the underlying changes to the mosaic composition.^{164,206} SEI with FEC is found to have only 12.5 at% F versus 24.9 at% without FEC after two activation cycles. This is later explained by the proposed possible reduction mechanisms for FEC, depicted in Figure 4.4.1. The first reduction pathway to (c) results in defluorination to LiF and poly(vinyl carbonate). This

pathway is similar to those previously proposed which assume a similar polymerization reaction as VC, with the additional benefit of LiF formation. The impact of this SEI polymerization reaction is a Si SEI that breathes in 1.3 nm amplitudes while lithiation and delithiation without FEC results in > 6 nm changes to SEI thickness. Without FEC, additional LiPF_6 decomposes to form LiF with each cycle, while C-O functionalities from FEC act as a polymeric SEI precursor. FEC changes the composition of the SEI in Si-based systems by minimizing salt and solvent decomposition. It preferentially reduces at 1.1 V vs. Li^+ due to its low LUMO and acts as a Si SEI precursor that breathes with each lithiation/delithiation.¹⁶⁴

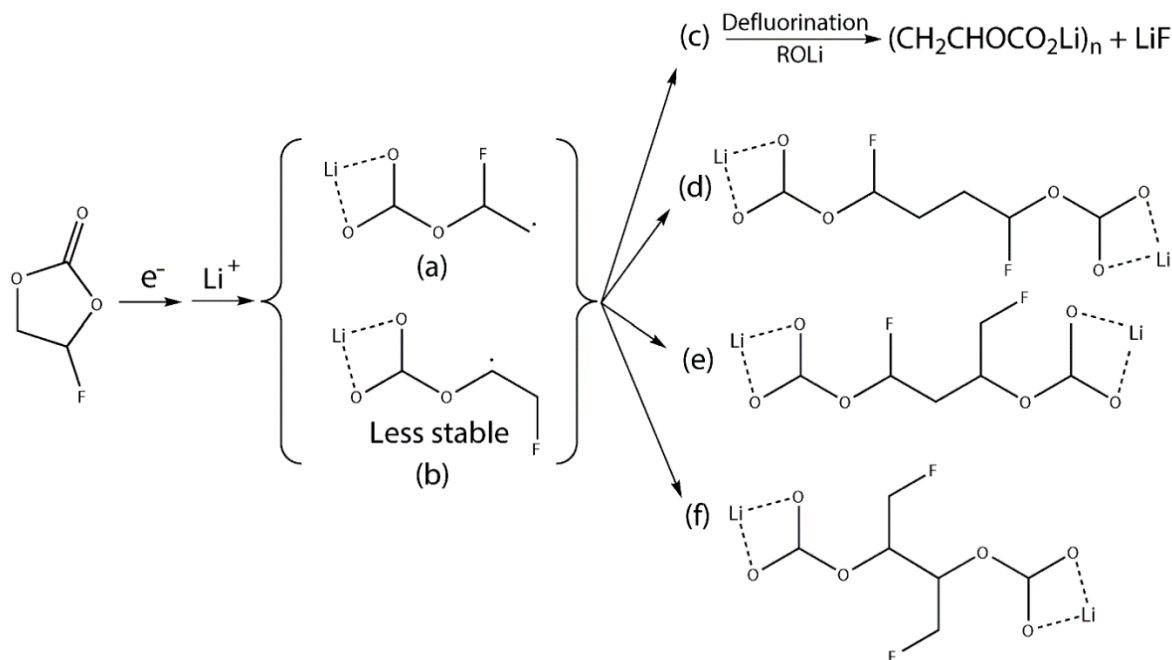
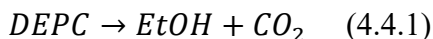
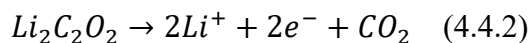


Figure 4.4.1. Proposed reduction paths for FEC. Radicals (a) and (b) are formed by reduction of the most positively charged carbon atom and lead to the cleavage of the five-membered ring. The radicals either defluorinate to form LiF and poly(vinyl carbonate), a similar reduction pathway to VC, or the three dimers given (d – f).²⁰⁶

After careful validation of the baseline additive package, other species such as diethylene pyrocarbonate (DEPC), lithium nitrite (LiNO_3), and diethyl sulfate (DTD) were investigated to improve the SEI formation on the Si Composite and NMC electrodes. DEPC is unique as a pyrocarbonate additive with a passivating mechanism unlike any of the other additive species in this study. The decomposition mechanism for DEPC as proposed by Chevrier *et al.* is given below with the key reductive product being carbon dioxide (CO_2):²⁰



This mechanism is similar to various pyrocarbonate additives tested for graphite in the 1990s and early 2000's, such as dimethyl pyrocarbonate (DMPC).^{209,210} However, previous efforts investigating CO_2 -forming additives for negative electrodes was abandoned after Aurbach demonstrated the use of EC as a more successful SEI former on graphitic electrodes in 1994.²¹¹ Only recently was the impact of CO_2 on silicon electrodes re-examined by the 3M research group and in a patent by Sanyo Electric Co Ltd.^{46,212} Lithium oxalate oxidation originating in the cathode as a sacrificial salt, adopts a similar SEI formation strategy for Si based electrodes. The mechanism as proposed by is included below:¹⁷⁹



The renewed interest in CO_2 -based additives for Si based electrodes is complicated by the indeterminate effects of CO_2 reduction. A long list of benefits including (i) LiOR, H_2O , and H^+ scavenging to form lithium formate and lithium carbonate, (ii) reduced trans-esterification of linear carbonates, and (iii) formation of a semi-insoluble and dense lithium carbonate based SEI are all attributed to CO_2 reduction.¹⁷⁸ The net result seems to be a synergistic effect, particularly with FEC, during continuous CO_2 reduction which abruptly ends when the CO_2 source is exhausted.^{20,179} One explanation is that the reduction products from CO_2 are partially soluble and

are therefore continuously consumed even when the Si electrode is not breathing during lithiation of delithiation. To test this hypothesis, DEPC was tested with 5 vol% in EC:DEC based electrolyte and NMC532||SiGr cells. The cycling results compared to the baseline additive combination with 10 wt% FEC + 1 wt% VC and a cell without additives are given in Figure 4.4.2. In Figure 4.4.2 (a) the volumetric energy density of the cells is given and all three cells start at approximately 610 Wh L⁻¹ in the first cycle which drops to 503, 551, and 548 Wh L⁻¹ after activation for the cell with DEPC, with baseline additives, and without additives, respectively. After 100 cycles at C/2, the cells retain 375, 361, 120 Wh L⁻¹ which corresponds to 75, 66, and 22 % energy retention, respectively. However, the energy density curve of the DEPC cell is particularly unique compared to the other systems which corresponds closely with the coulombic efficiency in Figure 4.4.2 (b), but not with any voltage hysteresis in Figure 4.4.2 (c). Namely, the cell shows a sinusoidal retention of energy density at C/2 which reaches a maximum of 550 Wh L⁻¹ after 50 cycles. This is higher than the initial capacity at C/2 and also corresponds to the cycles with the lowest coulombic efficiency in the cell, 96 %. The gradual decrease in the coulombic efficiency and increase in energy density most likely corresponds to consumption of DEPC which forms a temporary SEI for the first 60 cycles. After the DEPC is consumed, the energy retention of the cell, the coulombic efficiency, and the voltage hysteresis decay in unison. Every parameter except the coulombic efficiency drops precipitously. However, the coulombic efficiency never exceeds 99.0 % before or after DEPC is consumed in the cell.

The lithiation/delithiation curves in Figure 4.4.2 (d) indicate retained capacity between the 50th and 6th cycle. Differential capacity plots in Figure 4.4.2 (e) show no significant overpotential of the NMC532 delithiation except for strong SEI formation above 4.2 V in the first cycle. Previous work indicates that pyrocarbonates can work synergistically with FEC in Si based

electrodes.^{20,46} Additional experiments were performed using DEPC in the fluorinated system with FEC solvent but the electrolyte was unstable. After storing for half a week, the electrolyte had turned a dark brown and partially evaporated. It is understood that DEPC will dissolve certain plastics including polycarbonate containers. Pouch cells with the fluorinated electrolyte and DEPC additive experienced gassing issues that were unsuitable for future characterization. It is suspected that the DEPC partially hydrolyzed due to exposure to moisture and/or improper storage above the recommended 2 – 8 °C.

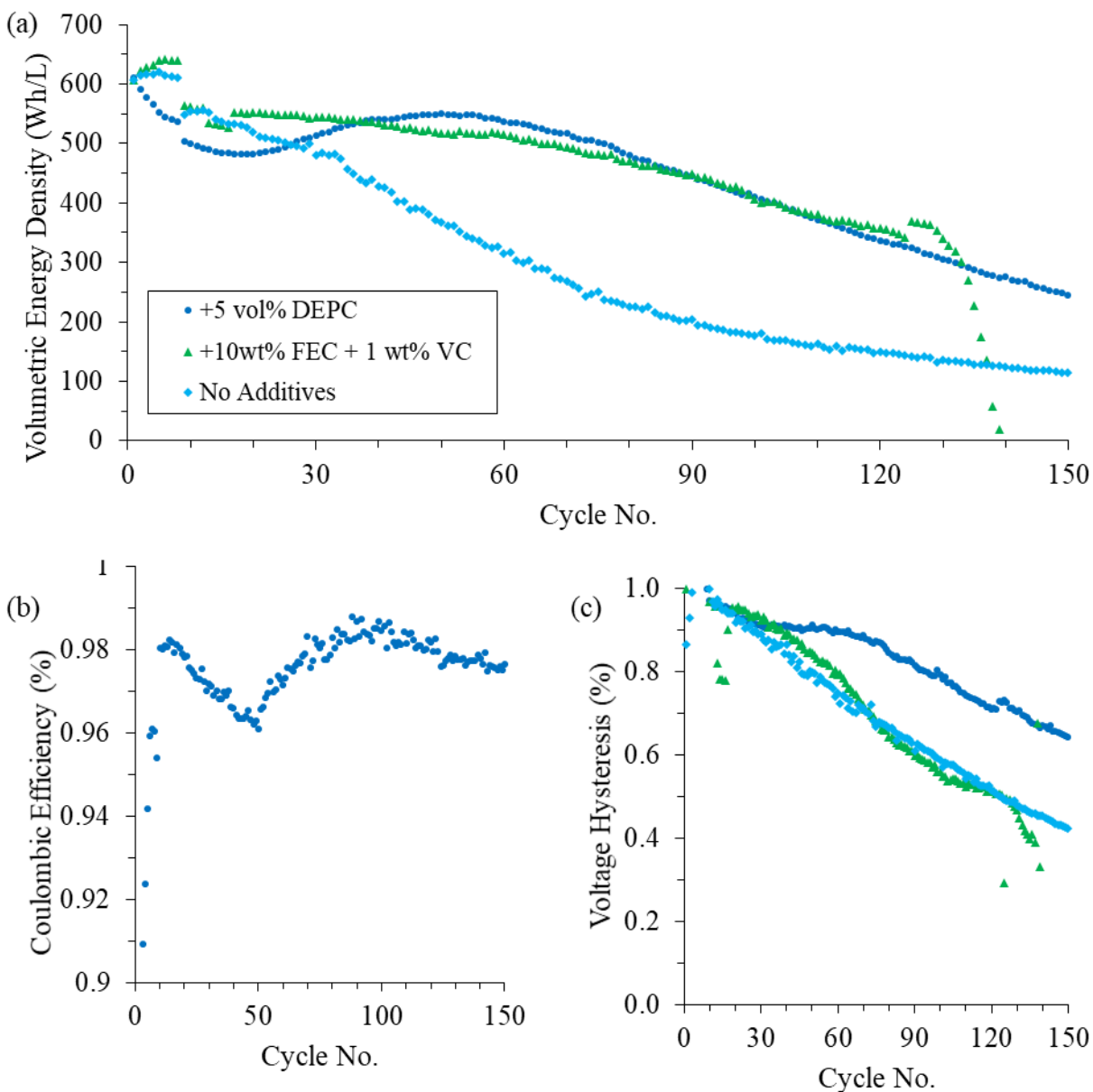


Figure 4.4.2. (a) Volumetric energy density, (b) coulombic efficiency, and (c) voltage hysteresis of NMC532||SiGr full cells with 1 M LiPF₆ in EC:DEC (50:50 wt%) baseline electrolyte (light blue) versus 10 wt% FEC + 1 wt% VC additive combination (green) and 5 vol% DEPC additive (dark blue).

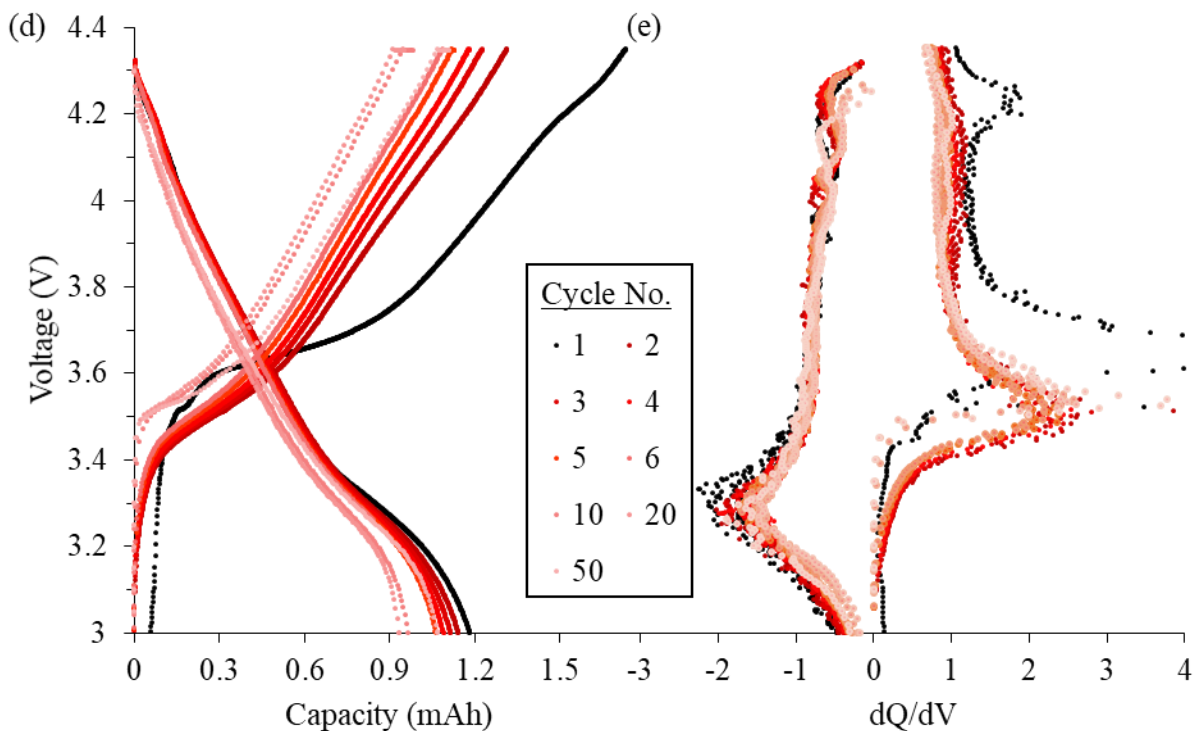


Figure 4.4.2. (d) Charge and discharge voltage profiles of the 5 vol% DEPC additive cell with corresponding (e) differential capacity analysis.

Lithium nitrate (LiNO_3) is a well-established battery material but was only recently discovered and implemented as a successful additive for Li (metal)||Sulfur systems, and then Si electrodes by Aurbach and coworkers.^{21,213} The later overlaps with the limited publication trail from Amprius, Inc. a company specializing in full cells with Si nanowire electrodes and high gravimetric energy densities. Although it is well known that SEI is hugely impacted by solvent reduction, these works use *ex situ* XPS and FTIR to characterize the changes in surface chemistry of systems with and without LiNO_3 . Not only did the authors find significant benefits for cycling Si electrodes in 1,3-dioxolane (DOL) solvent systems, rather than alkyl carbonate (e.g. EC and DMC), but the fast reduction of the nitrate additive significantly improves performance. The carbon content of the SEI decreases with the additive and the oxygen content increases.

Furthermore, the additive results in surface films with 30% more organic fluorides rather than LiF (40 % to 70 %). Overall, the authors concluded that LiNO_3 helps form Li_2O and Li_xNO_y species which ensure a thinner and more polymeric SEI.

In this study, LiNO_3 is tested in the industry standard alkyl carbonate system, EC:DEC (50:50 wt%), with and without a baseline additive package consisting of 10 wt% FEC + 1 wt% VC. Cyclic voltammograms and impedance spectra of the additive package are first tested in half cells with the Si composite in Figure 4.4.3. The reduction peak of EC at 0.95 V is visible in the potential window of the voltammogram as well as a large reduction peak at 1.5 V. The later can be attributed to lithium nitrate while the peak at 1.3 V is associated with FEC decomposition. Previous work by Nguyen and Lucht,¹⁹⁹ proposed that LiNO_3 preferentially reduces before FEC and forms a lithium carbonate-rich SEI. Impedance spectra of the same cells indicate higher impedance with lithium nitrate and FEC. In conclusion, the impact of lithium nitrate appears to be reduced reduction of FEC which could result in higher initial impedance. These results are next translated to full cells with NMC532 positive electrodes.

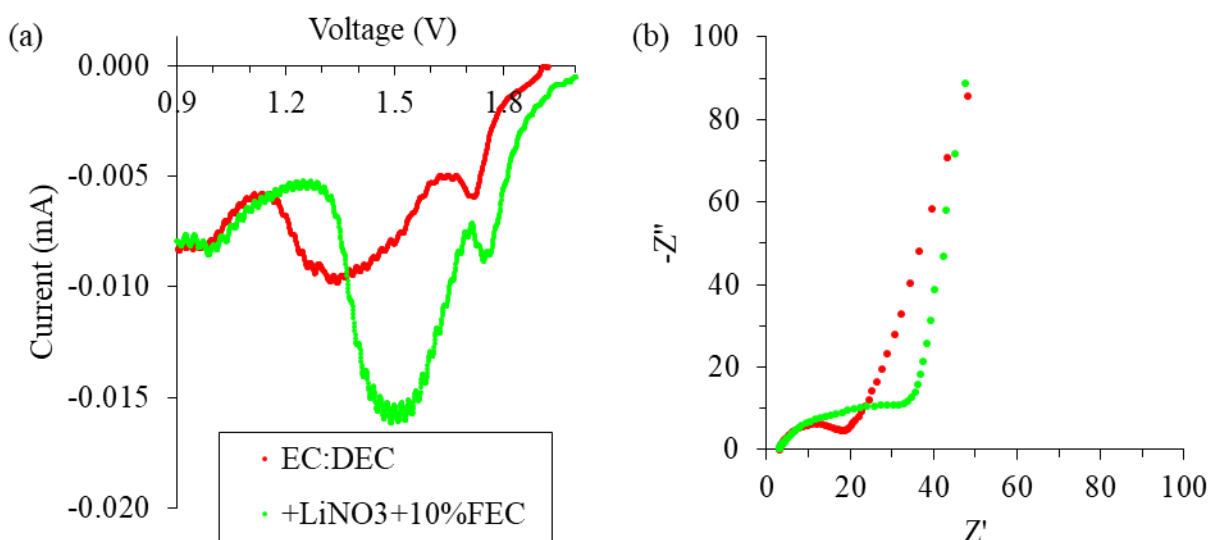


Figure 4.4.3. (a) Cyclic voltammetry and (b) impedance spectra of Si composite half cells with and without 1 wt% LiNO₃ + 10 vol% FEC additives.

Surprisingly, the performance of NMC532||Si composite full cells with 1 wt% LiNO₃ additive + 10 vol% FEC is fairly consistent to cells with only 5 wt% FEC in Figure 4.4.4. After 200 cycles, the cell without LiNO₃ retains 1.62 mWh discharge energy while the cell with retains 1.69 mWh of energy (after 196 cycles). One thing to consider when comparing these cells, the Si composite with LiNO₃ is slightly thinner with lower mass loading than the cell without. This results in a higher gravimetric and volumetric performance, but also makes a direct comparison between the two systems more challenging. In particular, since the n/p ratio in full cells with Si electrodes is a sensitive parameter, differences in performance could be the result of differences in between the negative electrodes. However, this should not impact the rate performance in the first 16 cycles since the both full cells have > 1.3 n/p ratios, with the C-rate determined by the positive electrode loading. Nevertheless, the coulombic efficiency of the cell with LiNO₃, which averages 99.63 % in the first 100 cycles at C/5 and 99.47 % for all cycles at C/5, is significantly higher than any previously tested additive package. In addition, by normalizing the capacity to the first C/5 cycle after the rate performance protocol (17th cycle), the full cell with LiNO₃ retains 80% of its capacity for 100 cycles between 4.3 - 3.0 V. And, achieves 99.77 % averaged retained capacity per cycle in that window. These metrics indicate that LiNO₃ is a highly promising additive for NMC||Si composite full cells. In particular, the coulombic efficiency in stainless steel coin cell shells, without an Al-coated top cap, is significantly more stable than additive packages with FEC and/or VC. Regrettably, LiNO₃ was tested in the mixed ionic liquid system to little benefit and was never further pursued in the flame retardant fluorinated system. This additive remains one of the most appealing for synergistic improvement in carbonate systems with FEC.

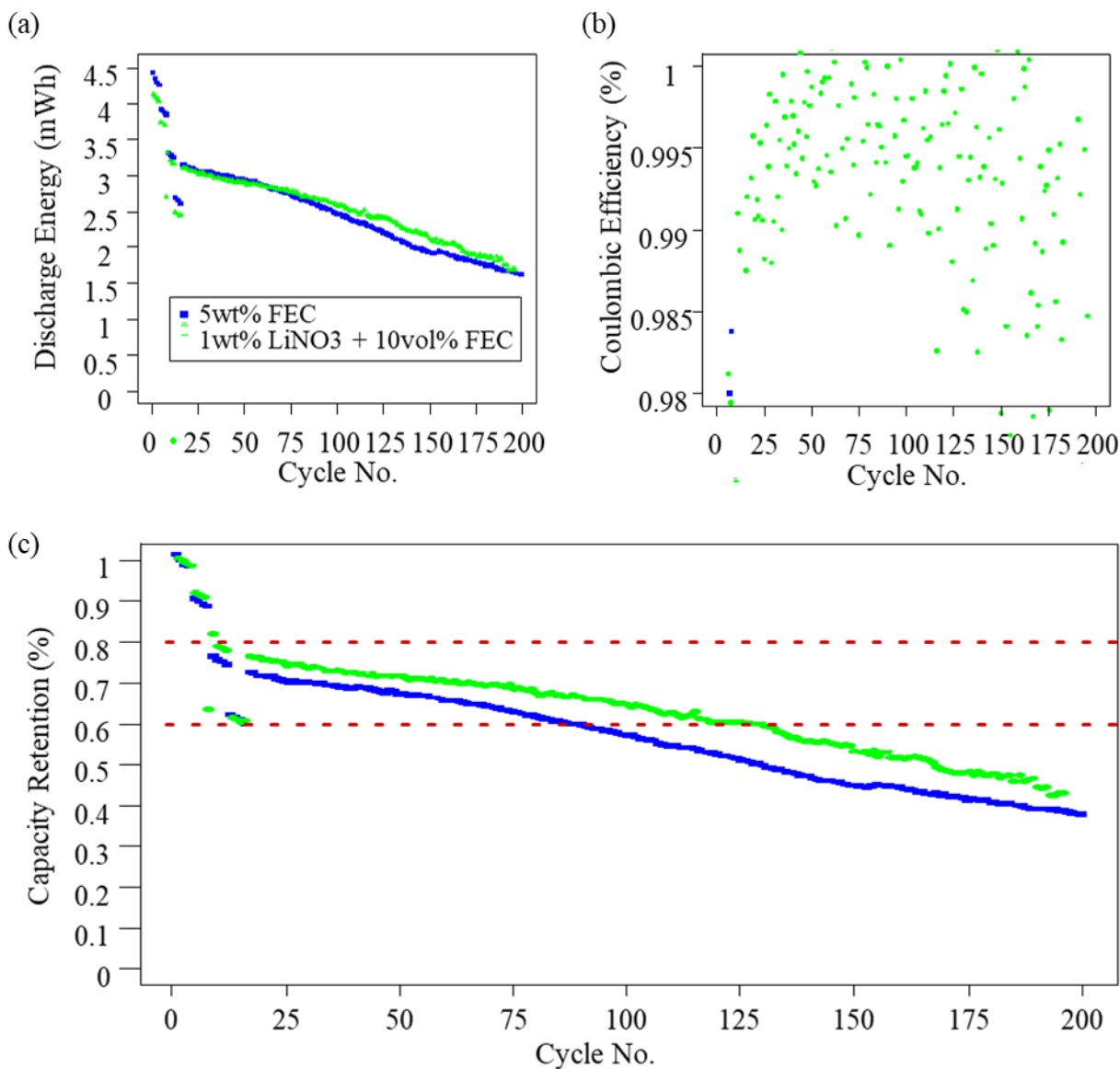


Figure 4.4.4. (a) Discharge energy, (b) coulombic efficiency, and (c) capacity retention of NMC532||Si composite full cells over 184 cycles at C/5 after sixteen preliminary rate performance cycles between C/20 and C/2.

Ethylene sulfate (also known as 1,3,2-Dioxathiolane-2,2-dioxide or DTD), tris(trimethylsilyl) phosphite (TTMSPi), and lithium bis(fluorosulfonyl)imide (LiFSI) were investigated to improve the performance of Si-containing full cells. All three performed poorly in CCCV coin cell tests with NMC||SiGr electrodes. DTD additive was first tested by adding 1 wt%

to 1 M LiPF₆ in EC:EMC (3:7 wt ratio) with 5 wt% FEC. These cells performed poorly and after one week, the electrolyte had precipitated salt and turned brown. It is suspected that DTD prematurely hydrolyzed in transit and performed poorly due to the quality of the material.

1.0 M LiFSI was used in the fluorinated electrolyte system, HFE:FEC:DMC (2:2:6 wt ratio), with 0.1 M LiPF₆ to ensure a stable SEI on the graphitic active material. The performance of the cells relative to the baseline system without any additives is given in Figure 4.4.5. The baseline system retains 80 % of its capacity at C/5 after 69 cycles while the system with LiFSI lasts less than half as long, for 26 cycles. The average coulombic efficiency of the LiFSI system is only 99.24 % at C/5 and in the first 30 cycles at C/5, it is 99.02 %. This is significantly lower than previous systems tested with the NMC and Si composite electrodes. Similarly, the average retained capacity per cycle of the LiFSI system is 99.29 % after 100 cycles while the no additive system is 99.59% after 250 cycles.

Previously, LiFSI was found to form a more oxygen-rich SEI, with less SiO_xF_y, using depth-resolved photoelectron spectroscopy (PES) measurements of nanosilicon electrodes.²¹⁴ These results have been confirmed in full cell configurations using NMC532 by Abraham's group at Argonne National labs after some minor electrolyte optimization.²¹⁵ While the performance of the LiFSI-FEC and LiPF₆-FEC systems was very similar, from differential capacity analysis, Trask and coworkers found that the potential for FEC decomposition varied by 160 mV for the two systems. The LiFSI-FEC system reduced FEC at 1.2 V vs. Li/Li⁺, while the LiPF₆-FEC reduced FEC at 1.04 V vs. Li/Li⁺. This difference in the reduction potential indicates a change in the FEC solvation structure based on the electrolyte salt that contradicts the conventional wisdom that the electrolyte salt is not expected to greatly impact SEI formation.^{113,164,197} The results in Figure 4.4.5 cannot corroborate in improvement in NMC||SiGr performance by using LiFSI salt. Two key

changes to the system could be culpable for this poor performance, namely, the higher wt% of Si additive and the potentially detrimental addition of 0.1 M LiPF₆. The 1M LiFSI+0.1MLiPF₆ system also performs atrociously in full cell voltage drop and LSV measurements using an Al||LiCu configuration. The poor performance in these additional tests indicates some underlying instability of the LiFSI salt rather than the Si additive. Once again, it is possible that the LiFSI material is compromised by hydrolysis of the source or corrosion of the Al current collector (> 3.3 V vs. Li/Li⁺). However, the later was supposed to be mitigated by the addition of 0.1 M LiPF₆. The LiFSI salt was identified as a promising replacement for LiPF₆ salt in LIBs is due to its higher conductivity, better thermal stability, and better storage stability (against hydrolysis).²¹⁶ It is disappointing that the performance of LiFSI in this system is so poor relative to the baseline fluorinated electrolyte.

The additive TTMSPI and other silyl species was first discovered in the patent portfolios of the Sumitomo Chemical Company (Japan) and Wildcat Discovery Technologies (California, USA) by the Dahn group.^{217,218} 2 wt% TTMSPI additive was tested in the fluorinated system with 1 m LiPF₆ salt. From the voltage profile of the cell in Figure 4.4.5, the additive reduces at ~ 2.7 V to form a film of the positive electrode.^{184,217,219} However, in this system, the performance does not improve with TTMSPI and therefore the approach was soon abandoned.

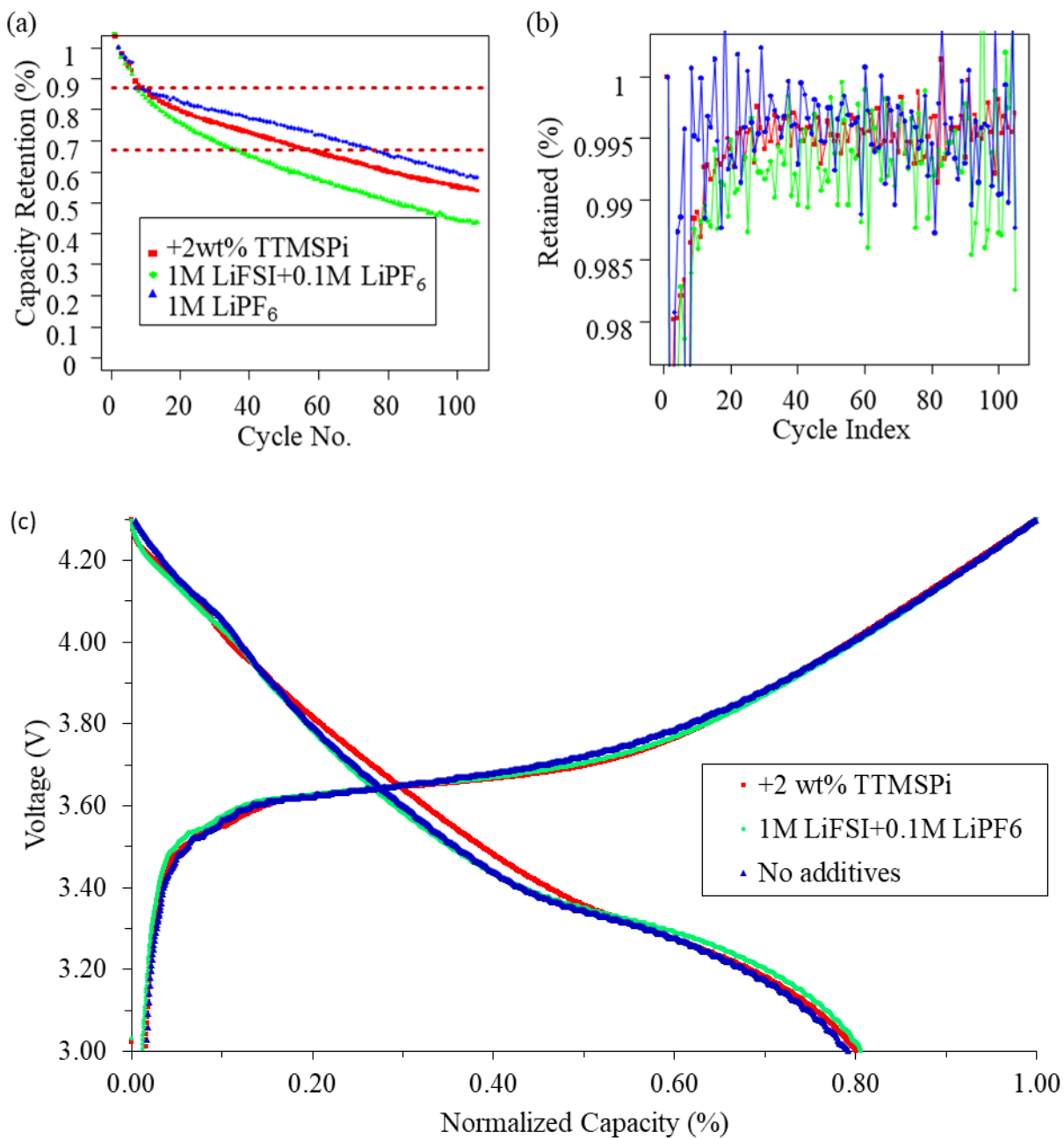


Figure 4.4.5. (a) Capacity retention and (b) retained capacity per cycle of NMC532||SiGr cells in HFE:FEC:DMC (2:2:6 wt ratio) with 1 M LiFSI + 0.1 M LiPF₆ (blue), 1 M LiPF₆ with no additives (green) or with + 2 wt% TTMSPI (red). (c) Voltage vs. capacity curves of the first cycle of the same cells.

Lithium difluoro(oxalato)borate (LiDFOB), also known as lithium oxalyldifluoroborate (LiODFB), was first reported as a LIB salt by Sheng Shui Zhang from the Army Research Lab in 2006. The chemical structure of LiDFOB is similar to lithium bis(oxalate)borate (LiBOB), with one oxalate subunit, and lithium tetrafluoroborate (LiBF_4), with two fluorine sigma bonds. But, compared to its two parent compounds, LiDFOB shows a number of distinct advantages. For instance, it has much better solubility than LiBOB in linear carbonates which results in better rate and low temperature performance, and unlike LiBF_4 , the salt can form a stable SEI on electroactive graphitic surfaces.²²⁰ More recently, LiDFOB has been adapted as an electrolyte additive to form (i) a stable SEI with reduced interface impedance growth,²²¹ (ii) positive electrode passivation for reduced metal dissolution,²²² and (iii) a more compact negative electrode SEI. Reduction in graphite half cells occurs near 1.7 V vs. Li/Li^+ , higher than other species in fluorinated and standard organic electrolyte, although it does not significantly suppress the reduction of the other solvents.^{222,223}

In this study, LiDFOB is tested in 2032 coin cells with NMC532 and SiGr (30:58 wt%) electrodes by CCCV, EIS, voltage drop, and impedance electrochemical tests. The n/p ratio of the cells is 1.26 and the baseline electrolyte is the fluorinated system from Section 4.3, 1.0 m LiPF_6 in HFE:FEC:DMC (2:2:6 wt ratio). After cycling between 4.3 – 3.0 V for 100 cycles at C/5 rate, as determined by the areal capacity of the positive electrode, with a C/20 trickle charge cutoff, the cells were disassembled and prepared for SEM and EDS characterization.

The CCCV results are given in Figure 4.4.6. The initial volumetric energy densities at C/5 of the cells from highest to lowest additive wt% are 776, 774, 741, 649, and 610 Wh L^{-1} , with corresponding initial coulombic efficiencies of 78.9, 79.4, 79.5, 56.0, and 76.8 %. The energy density of the full cell increases by 27 % with the addition of 4 wt% LiDFOB without impacting

the initial coulombic efficiency. However, the additional activation of the full cell leads to worse energy retention. In the first 30 cycles at C/5, in order of decreasing LiDFOB wt%, the cells lose 19.3, 15.9, 15.4, 11.4, and 10.2 % of their capacity, and, after 100 cycles, they retain 367, 431, 436, 403, and 424 Wh L⁻¹. Noticeably, the cells with 2 and 3 wt% LiDFOB retain the most energy after 100 cycles. This is manifested in the average coulombic efficiency of each system as well as the average capacity retained per cycle. In order of decreasing LiDFOB wt%, the average coulombic efficiencies are 98.9, 99.3, 99.1, 92.5, and 99.2 %, while the average capacity retained per cycle is 99.2, 99.4, 99.3, 99.6, and 99.7 %. Previous work out of Argonne National lab determined that beyond 3 – 5 wt% LiDFOB, the benefits of the additive plateaued and the passivation reaction saturated.²²¹ However, in this system, with SiGr negative electrodes, the coulombic efficiency of the 3 wt% LiDFOB cell is the highest, while the 4 wt% system drops in performance, precipitously. This indicates that the LiDFOB species functions successfully as an interface and/or interphase former rather than contributing positively to the bulk transport properties of the system. However, it is clear that the activation of cell improves significantly with the addition of even a low weight percent of LiDFOB, although the additional capacity made available is not easily retained. This is most notably embodied by the retained energy of the 2 wt% LiDFOB cell, which is better than the lower wt% systems as well as the higher wt% systems after 100 cycles. Previous studies provide evidence for a more compact SEI on graphitic surfaces which eventually leads to good power capability.²²¹ It can be hypothesized that as a bi-functional additive, LiDFOB enables additional capacity to be extracted from the positive electrodes and a thicker, more stable SEI on the negative electrode. This leads to the higher initial discharge capacity and energy, but also keeps the ICE relatively consistent between systems with varying weight percent.

Looking at the voltage hysteresis plot in Figure 4.4.6 (d), the 3 and 4 wt% systems suffer from significant fade over time. This can be attributed to the more comprehensive utilization of the SiGr electrode and repeated expansion of the Si nanoparticles. The additional available lithium results in greater particle expansion, which leads to greater strain on the electrode and additional formation of $\text{Li}_{15}\text{Si}_4$, as seen in the differential capacity analysis from Figure 4.4.8 (c), which are all detrimental to the performance of Si-based electrodes. From the CCCV results, it is clear that the LiDFOB can significantly improve full cell activation. Additional experiments are conducted to identify the root cause and conditions for this improvement in performance.

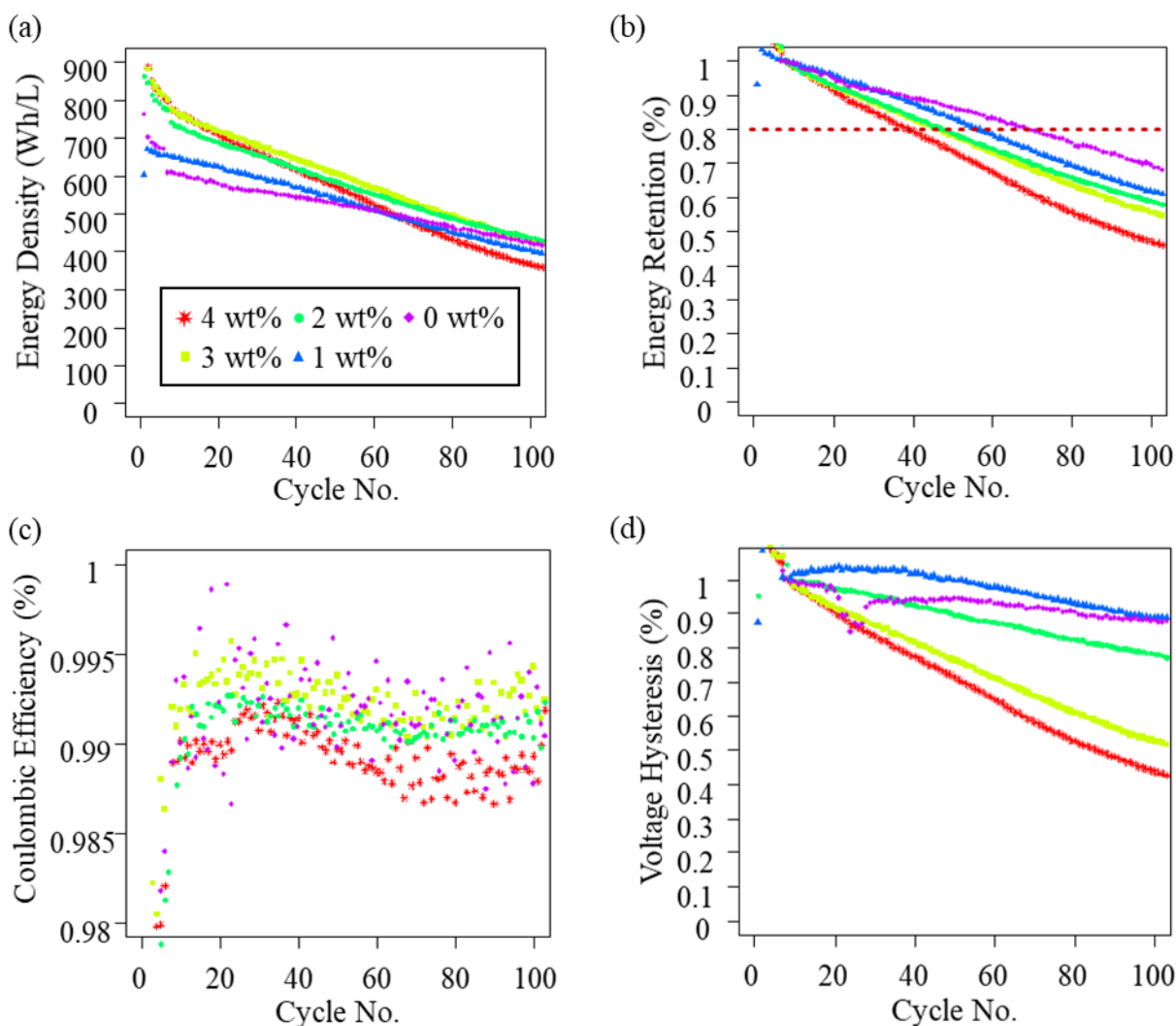


Figure 4.4.6. (a) Volumetric energy density, (b) energy retention, (c) coulombic efficiency, and (d) voltage hysteresis of NMC532||SiGr full cells in 1.0 m LiPF₆ in HFE:FEC:DMC (2:2:6 wt ratio) with 0, 1, 2, 3, or 4 wt% LiDFOB additive.

The voltage drop test results are presented in Figure 4.4.7. The test is conducted after activating the NMC532||SiGr full cells and forming a stable SEI. Coin cells are held at a tap voltage of 1.5 V for 24 hours before cycling at C/20 between 4.3 – 3.0 V for 1 cycle, and then charging and holding the cell at 4.3 V for 24 hours. The cells are stored at 20 °C with periodic measurements by EIS to determine the voltage drop and impedance spectra. This test useful for determining the stability of the electrodes as well as the electrolyte against parasitic reactions. Electrolyte with 1.0 m LiPF₆ in EC:EMC (3:7 wt ratio) is a common baseline in commercial LIBs with graphite electrodes. This system loses 403 mV over 624 hours of storage at 20 °C, as seen in Figure 4.4.7 (a). In comparison, the fluorinated electrolyte system from Section 4.3, with 1.0 m LiPF₆ in HFE:FEC:DMC (2:2:6 wt ratio), only drops by 268 mV. Already the system from Section 4.3 performs significantly better than the EC:EMC commercial standard, however it is expected that this can be improved by the addition of low weight percent, interface-improving additives. For example, by adding 2 wt% LiDFOB, the voltage drop is reduced even further to only 156 mV after 624 hours which is equivalent to approximately 0.25 mV/hr. In comparison, the fluorinated system with 3 wt% LiDFOB, 0.5 wt% BBF, and 1.0 m LiFSI + 0.1 m LiPF₆ drop by 259 mV, 183 mV, and 3.95 V after 624 hours. The LiFSI system in particular performs very poorly and loses 739 mV in the first 24 hours, while the voltage of the BBF system remains high, but the electrochemical performance was poor. It is likely that the LiFSI salt corrodes the Al coin cell top cap, even though the addition of 0.1 m LiPF₆ was intended to form a passivating AlF₃ layer.

From the voltage drop measurements in Figure 4.4.7 (a), the 2 wt% LiDFOB system performs the best after 624 hours of storage. The impedance spectra in Figure 4.4.7 (b) of the fluorinated system with and without 2 wt% LiDFOB after 24 and 624 hours of storage hint at the source of the improvement. While the impedance of the fluorinated system without any additives (No Add.) is 2 Ω less after activation, the rise in impedance is 800 % higher, up 8 Ω to 27.5 Ω . The 2 wt% LiDFOB cell only increases 1 Ω of charge transfer impedance to 22 Ω , and the Warburg diffusion resistance decreases after 624 hours of storage. This indicates that 2 wt% LiDFOB additive helps form a more resistive SEI after 1 cycle which is better retained after hours of storage, with less side and parasitic reactions. This is similar to previous reports of LiDFOB cells which form a thicker initial SEI which is more stable with better rate performance.^{220–224}

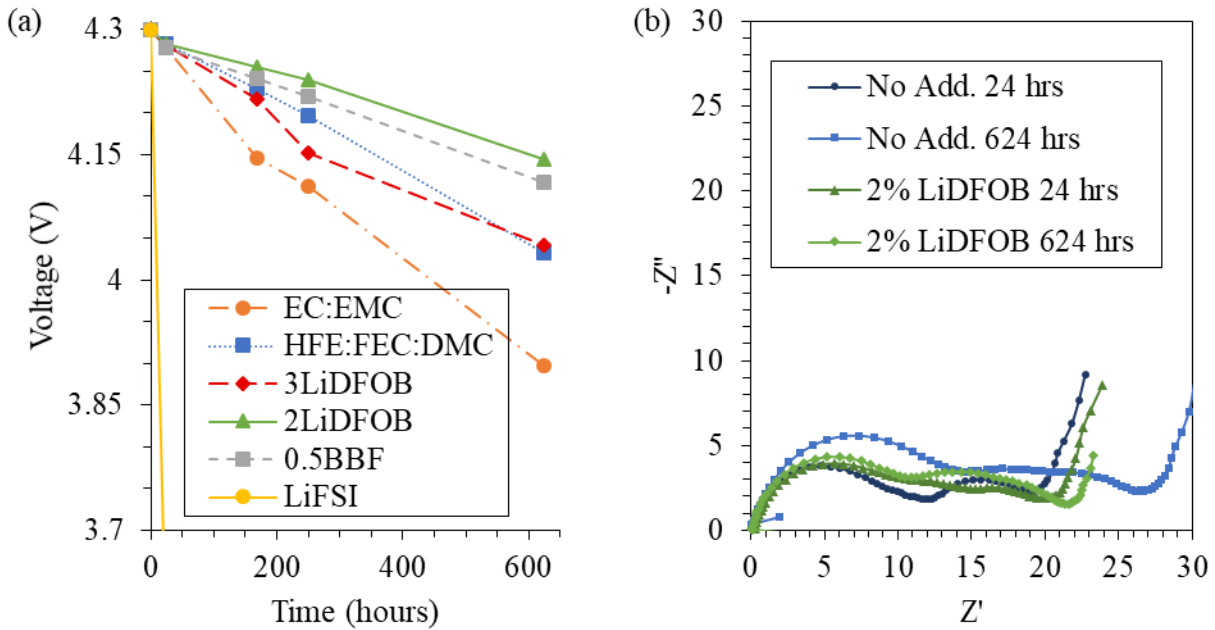


Figure 4.4.7. Results from the voltage drop tests of NMC532||SiGr full cells in various electrolyte systems. (a) Plot of the change in voltage over time of cells stored at 20 °C. (b) Impedance spectra of NMC532||SiGr cells with (green) and without (blue) 2 wt% LiDFOB additive in the fluorinated electrolyte system from Section 4.3.

Impedance tests are carried out next on NMC532||SiGr cells with and without 3 wt% LiDFOB in the fluorinated electrolyte system from Section 4.3. Coin cells are held at a 1.5 V tap voltage for 24 hours before cycling at C/20 up to 4.3 V and holding until a C/20 cutoff current. Then, the impedance of the cell is collected using a Biologic VMP3 multichannel system in a frequency range from 100 kHz to 0.1 Hz at approximately 20 °C. Subsequent measurements are conducted at 4.3 V in between cycling 1 cycle at C/20, 2 cycles at C/10, and 10 cycles at C/5. The contact resistance at high frequencies is removed to better compare the mid-frequency charge transfer resistances in a Nyquist plot format. The real charge transfer resistance at approximately 1 kHz, is also given as a table inset Figure 4.4.8 (a).

The impedance spectra after 14 cycles is similar to the results from the storage tests in Figure 4.4.7. While the SEI and charge transfer resistance is lower for the fluorinated system without additives after activation, the rise in resistance is significant over time. In comparison, the system with 3 wt% LiDFOB only slightly increases in SEI impedance from the first semicircle, and charge transfer resistance, the x-intercept of the second semicircle. The voltage profile of the cells and the corresponding crude differential capacity analysis in Figure 4.4.8 (b) and (c), respectively, indicate minimal differences in the lithiation and delithiation behavior of the full cell. The 3 wt% LiDFOB system retains its capacity better with 66 % retention after 50 cycles compared to 61 % by the system without the additive. However, one difference from the CCCV results in previous tests is the voltage hysteresis of the cell with 3 wt% LiDFOB. As noted in the differential capacity curves, the cell with 3 wt% LiDFOB does not experience additional voltage or capacity fade. This will be attributed to the cycling conditions of the impedance test. Rather than continuously charging and discharging, there is a resting period at 4.3 V which can explain the differences in performance.

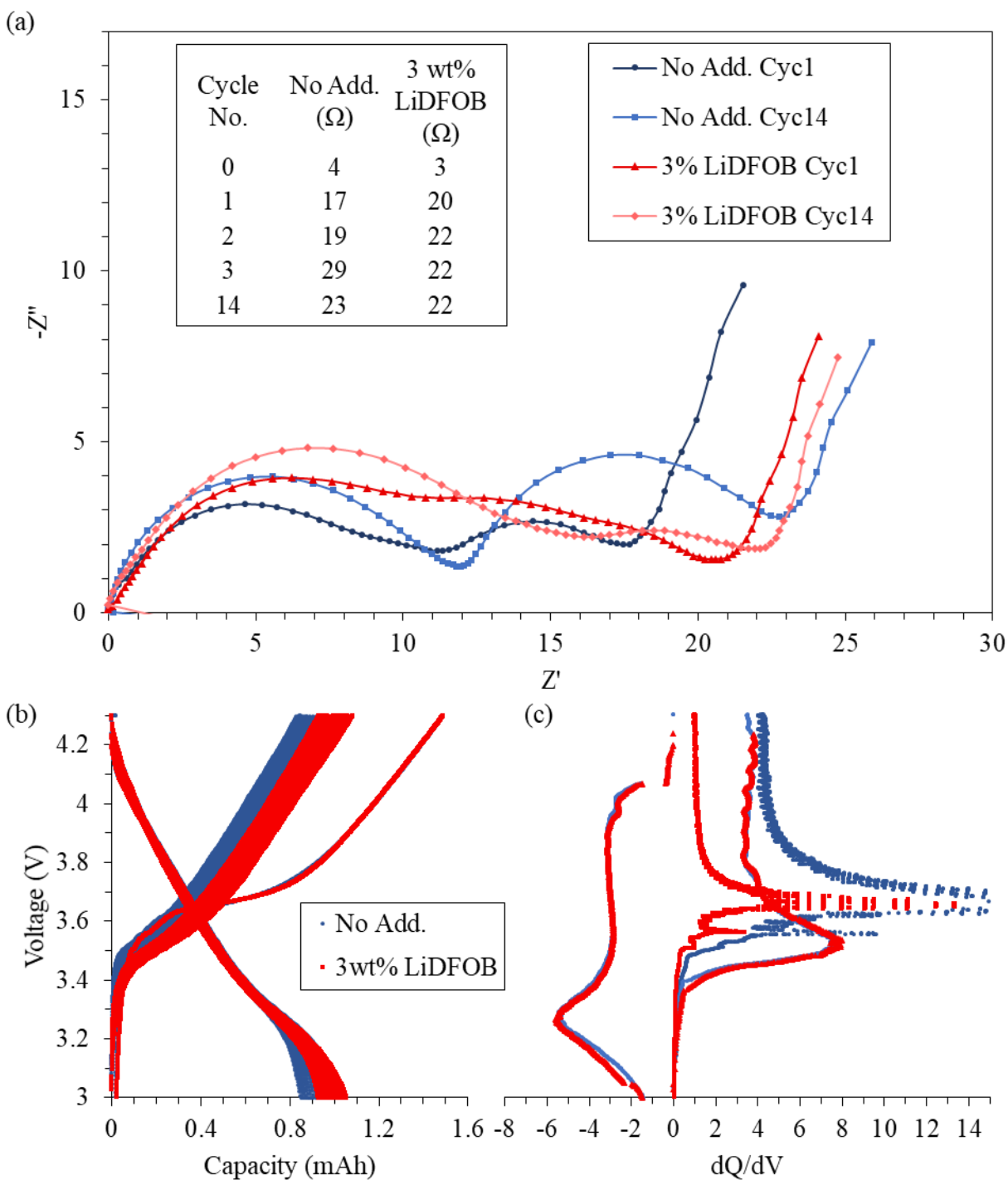


Figure 4.4.8. (a) Impedance spectra of NMC532||SiGr cells with (red) and without (blue) 3 wt% LiDFOB additive in the fluorinated electrolyte system from Section 4.3. (b) Voltage profile of the same cells after 14 cycles between 4.3 – 3.0 V.

Impedance, storage, and cycling tests indicated formation of a thicker and but also stable initial SEI with addition of LiDFOB to the fluorinated electrolyte system. This SEI withstands the expansion of the SiGr material better than the fluorinated electrolyte without additives and activates the full cell such that additional reversible Li^+ is available. The SEI of aged SiGr negative electrodes is characterized by SEM and EDS characterization in Figures 4.4.9 and 4.4.10. Cells with or without 3 wt% LiDFOB are investigated after 100 cycles at C/5. The EDS signatures of selected elements is included in Table 4.4.3.

Table 4.4.3. Energy of x-rays emitted from selected elements during EDS bombardment. Values in italics are $\text{L}\alpha$ values in keV.

	B	C	N	O	F	Al	Si	P	S	Cu
$\text{K}\alpha$ (keV)	0.183	0.277	0.392	0.525	0.677	1.486	1.739	2.013	2.307	8.04, <i>0.93</i>

A top-view image of the electrode without LiDFOB additive is shown in Figure 4.4.9 (a). The same image with the relative abundance of Si and C overlaid on top and the full EDS spectra for the ROI is inset in Figure 4.4.9 (b). Individual elemental maps of the Si, C, F, and B content are included in Figure 4.4.9 (c) – (f). Surprisingly, the electrode contains a relatively weak Si concentration and no B signal as indicated in the spectra. The spectra is largely dominated by a high concentration of F and lower, similarly weighted peaks for C, O, and P (1:1:~0.7). This indicates an SEI with lithium alkyl carbonates ($\text{CH}_2\text{-O}$ and O-(C=O)-O species), LiF, Li_xPF_y , and $\text{Li}_x\text{PF}_y\text{O}_z$ as observed in previous studies.^{223,225,226} The strong presence of FEC and HFE solvents further should contribute to the formation of LiF and other polymeric species in the SEI as described in Section 4.3. Proposed reduction mechanisms by Parimalam and Lucht for LiPF_6 and LiDFOB are also shown below in Equations 4.4.3 and 4.4.4, which correspond qualitatively with the EDS spectra in Figure 4.4.9 and 4.4.10.²²⁶

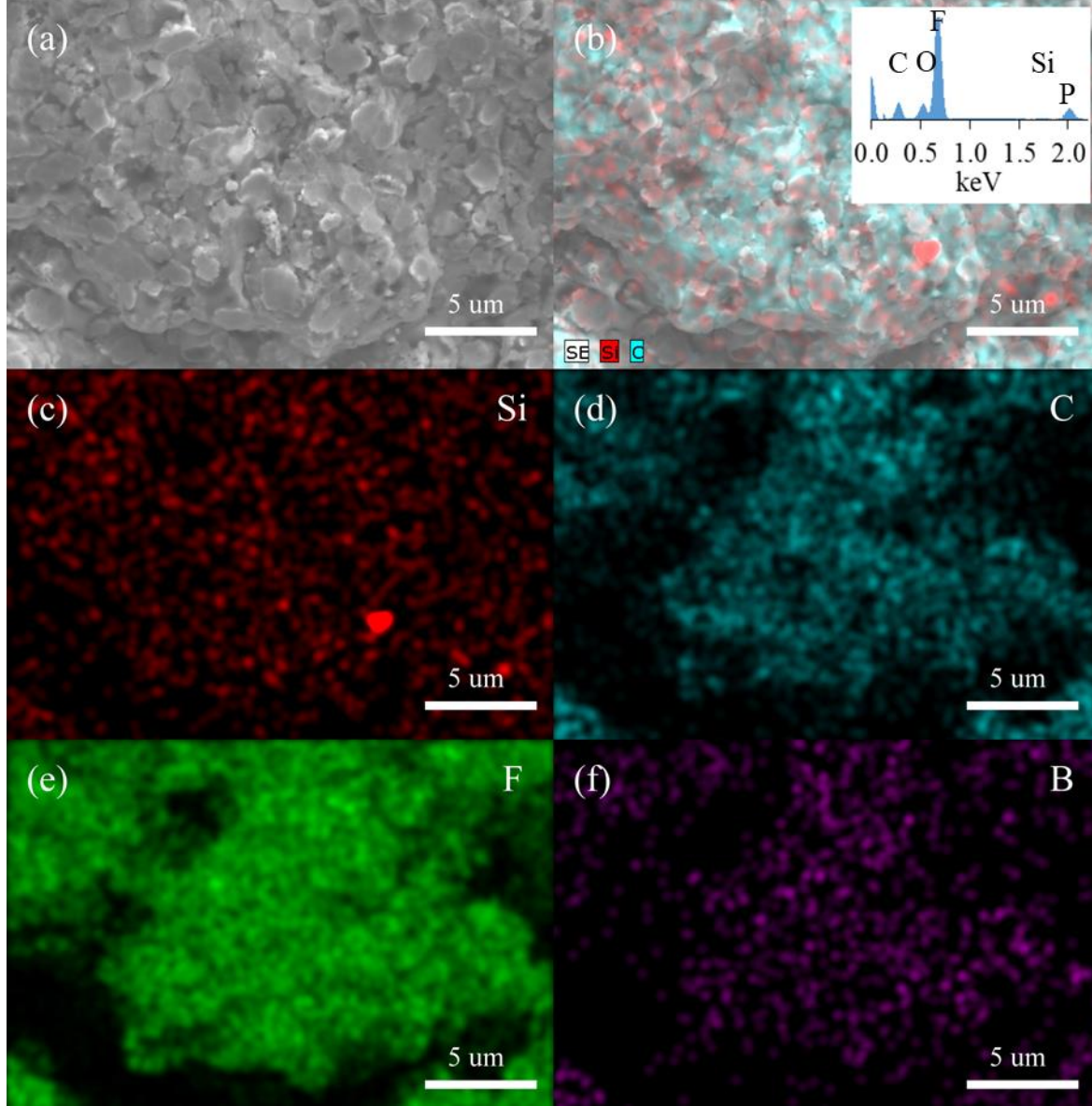
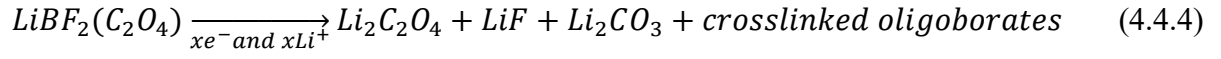
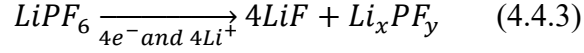


Figure 4.4.9. EDS images of the composite Si electrode from a fluorinated electrolyte cell without additives, 1.0 m LiPF_6 in HFE:FEC:DMC (2:2:6 by wt), after 100 cycles at C/5 between 4.3 – 3.0 V. (a) SEM image of the ROI. (b) The ROI overlaid with Si and C signals. Inset is the EDS spectra. (c – f) Elemental mapping of the Si, C, F, and B signals respectively.

The top-view SEM image of the electrode cycled with 3 wt% LiDFOB in the fluorinated system shows little resemblance to the electrode without the additive. In the SEM image in Figure 4.4.10 (a), without any overlapping elemental signals, it is immediately apparent that the surface of the electrode is grainy with varying degrees of conductivity, similar to reports of SEI on pure graphite electrodes with 1 M LiDFOB in EC solvent.²²³ Further characterization by NMR, GC-MS, IR-ATR, and XPS in this and subsequent reports indicate the decomposition of LiDFOB into lithium oxalate, lithium carbonate, lithium fluoride, and crosslinked oligomeric borates as given in Equation 4.4.2. In the elemental mapping images of Figure 4.4.10 (b) – (f) with C, Si, O, F, and B species, respectively, as well as the EDS spectra inset in Figure 4.4.10 (a), it is obvious that LiDFOB is responsible for stark differences in the SEI mosaic. In Figure 4.4.10 (b), graphite particles without Si nanoparticles are clearly observed with minimal SEI formation due to the strong concentration of C and weak concentration of other elements. Other areas of the electrode indicate a different balance of chemical species akin to the proposed reduction reaction for LiDFOB. In the elemental maps and EDS spectra, the concentration of F is still the greatest, but C, O, and Si have greatly increased in intensity, while P has significantly decreased. This indicates minimal decomposition of the LiPF_6 salt over 100 cycles at C/5, compared to the fluorinated system with a significant amount of FEC and HFE, but no additives. This increase in the Si concentration is also indicative of a largely thinner and more compact SEI. The higher ratio of C and O to F (1:2.5), may be further evidence that a polymeric and more oxygen-rich SEI is conducive for Si-containing electrodes.

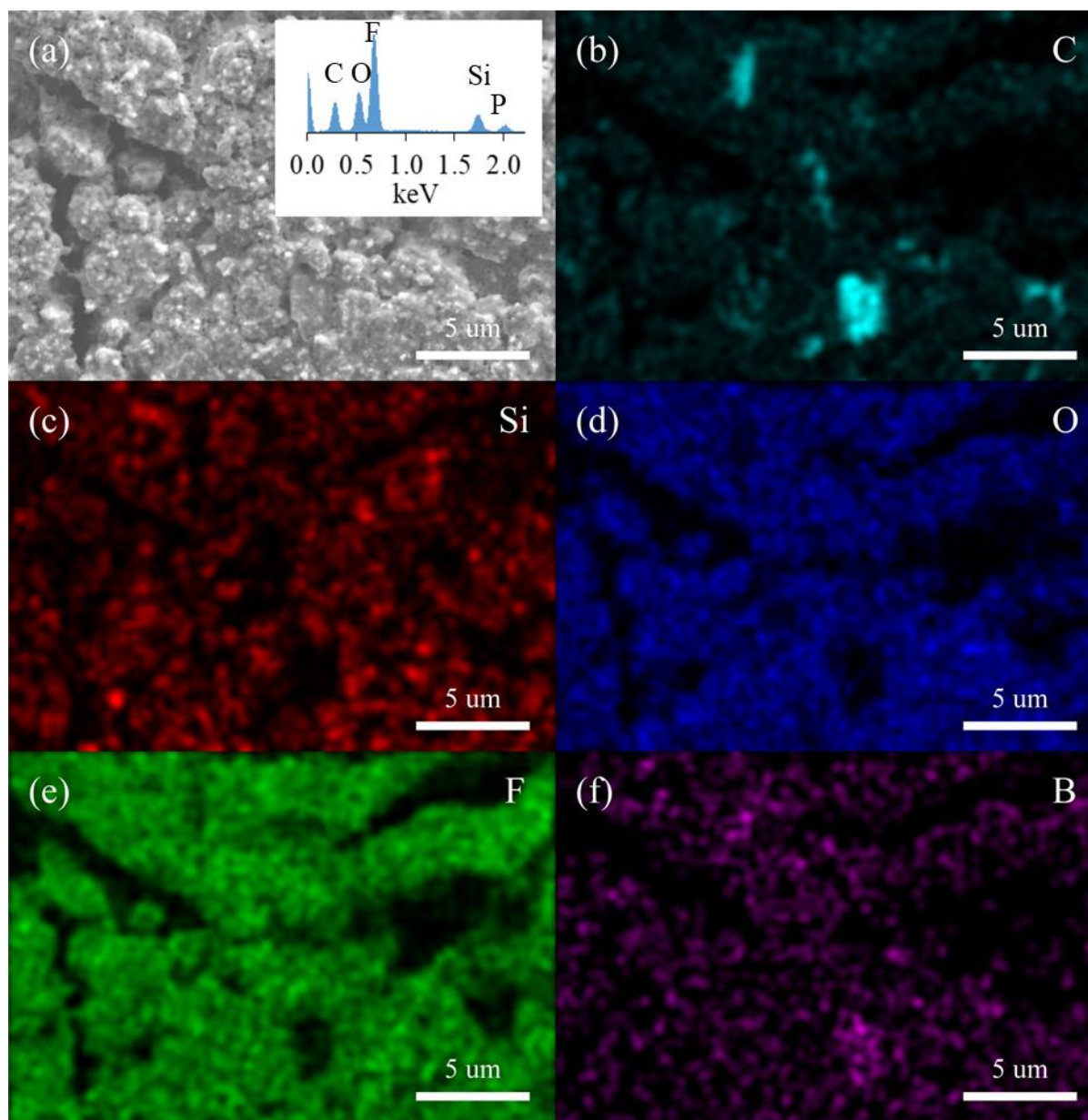


Figure 4.4.10. EDS images of the composite Si electrode from a fluorinated electrolyte cell with 3 wt% LiDFOB additive, 1 m LiPF_6 in HFE:FEC:DMC + 3 wt% LiDFOB (2:2:6 by wt), after 100 cycles at C/5 between 4.3 – 3.0. (a) SEM image of the ROI. Inset is the EDS spectra. (b – f) Elemental mapping of the C, Si, O, F, and B signals respectively.

The performance and characterization of the additives in this section lead to a number of surprising conclusions regarding the ideal interfacial properties and species for NMC||SiGr full

cell configurations. The pyrocarbonate additive, DEPC, forms a stable SEI in a carbonate system for 60 cycles but then decays quickly, afterwards. Furthermore, the electrolyte does not store well with DEPC and may cause acute corrosion of the polymer separator and other battery components. Lithium nitrate performed much better in full cell configurations with an average coulombic efficiency of 99.63 % in the first 100 cycles at C/5, significantly higher than any previously tested additive package. At C/5, the cell also retains 80 % of its capacity for 100 cycles between 4.3 – 3.0 V. It would be worthwhile to test this additive in the flame-retardant, fluorinated system both with and without LiDFOB. LiDFOB was tested to great success in the fluorinated electrolyte system. Impedance and storage tests indicate a stable SEI was formed on the Si composite electrode. Further characterization by SEM and EDS indicate that a more oxygen-rich and polymeric SEI forms on the electrode which explains the strong electrochemical performance. An additive package consisting of 2 to 3 wt% LiDFOB in the fluorinated electrolyte achieves the highest energy output for the NMC532||SiGr system with 741 to 774 Wh L⁻¹ volumetric energy density and between 99.3 to 99.4 % average coulombic efficiency, respectively.

Chapter 5: Negative Electrode Hosts with High Alkali Wettability

Lithium metal electrodes are some of the most appealing high energy density chemistries due to their high specific capacity and low redox potentials. However, the infinite volume change and dendritic behavior in alkali metal electrodes leads to low Coulombic efficiency and short-circuit issues that significantly hamper renewed efforts at commercialization. This section describes the stable and dendrite-free alkali metal electrodes made by thermally pre-loading molten Li or Na into a three-dimensional (3D) framework with high alkali wettability. This work was published in *Advanced Energy Materials* with co-first authors Dr. Zhang and Dr. Wang.²²⁷ The most critical failure mechanisms of metallic Li anodes are thoroughly examined via ex-situ SEM. In the mechanically robust 3D framework, carbon fibers (CF) serve as an electrical highway that provides fast charge transfer for the redox reaction. Through a facile solution-based process, a SnO₂ coating is introduced to modify the poor wetting behavior of the carbon framework and drastically improve both the electrochemical performance and reliability.

The kinetic barrier to adhesion of molten alkali metals on the CF framework is improved by the mixed reaction with SnO₂. The growth of dendrites is effectively repressed under the decreased local current density of the 3D framework with improved alkali wettability. In stark contrast to its bare Li metal counterparts, the 3D Li-CF composite electrode exhibits excellent long-term cycling performance (744 hr at 1 mA cm⁻² and 120 hr at 3 mA cm⁻²) with a stable stripping/plating profile and low overpotential (30 mV at 1 mA cm⁻² and 92 mV at 3 mA cm⁻²) in carbonate-based electrolyte without additives. In full-cell configurations with LFP cathodes, the Li-CF electrode shows reduced polarization and 90 % capacity retention after 500 cycles in traditional carbonate electrolyte. Comparable improvements are also observed in 3D electrodes for Na metal batteries. Our findings on a stable 3D carbon framework with improved wetting behavior

provide significant practical implications for achieving safe and commercially-viable alkali metal anodes.

Carbon surfaces have poor inherent affinity with pure molten Li, hence a conformal SnO_2 coating on each CF is critical to improve the wetting of molten alkali metals and form the Li/Na-CF composite.²²⁸ Figure 5.1a illustrates the two-step fabrication process of the Li-CF composite. In this case, a conformal SnO_2 layer (33 - 50 wt%) is applied to the 3D CF framework by a solution-based method to improve the affinity between CF and molten Li metal. Then, the composite is activated by thermal infusion of molten Li into the SnO_2 -CF disk within 27 seconds. The fast intake of Li by the 3D CF framework is indicative of the improved wettability and mixed reaction that occurs with the SnO_2 coating.

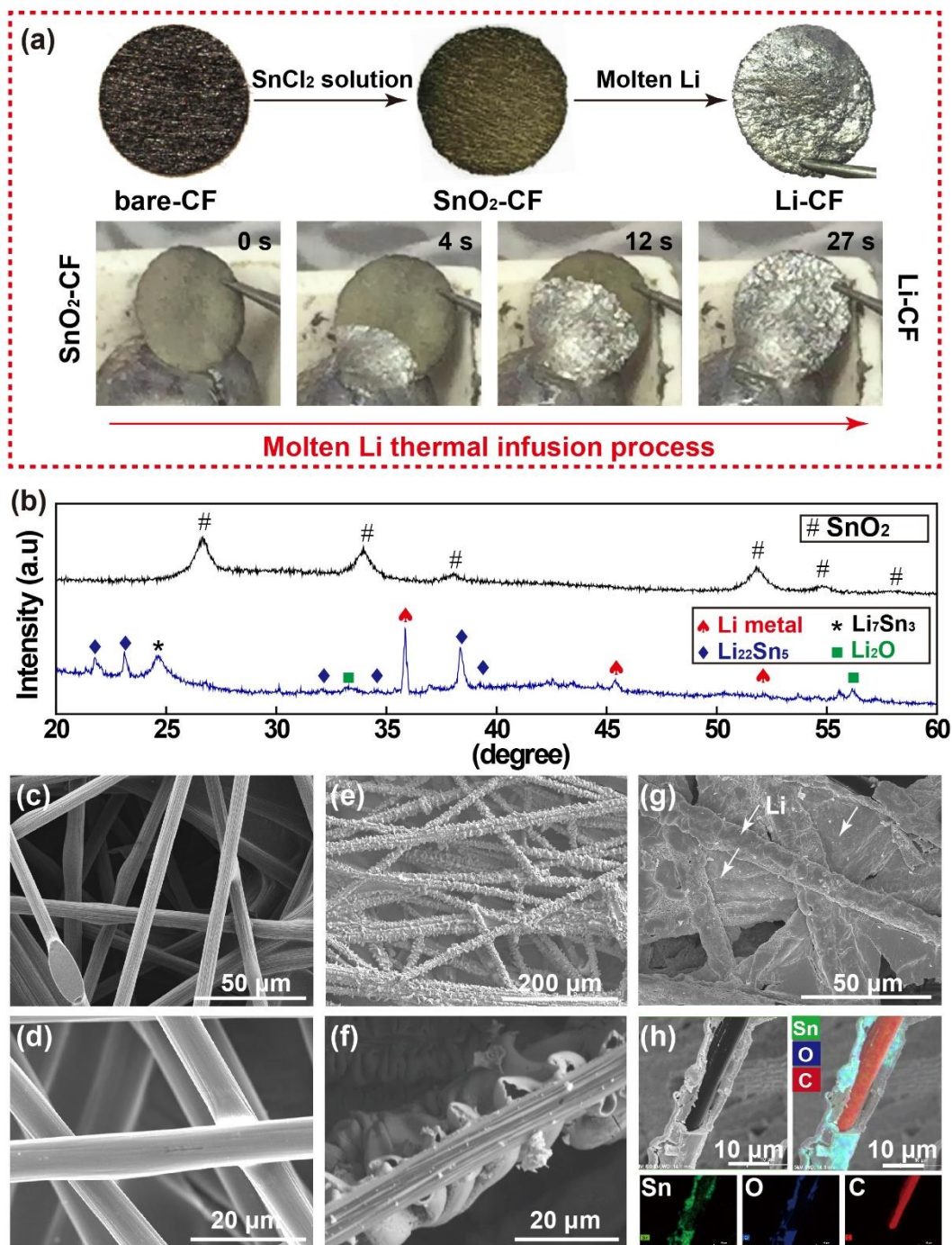


Figure 5.1. The fabrication process and microscopic characterization of the Li-CF composite. (a) Digital images of the bare CF (left), SnO_2 -CF (middle) to Li-CF composite (right) throughout the 27 seconds thermal infusion process of molten Li. The diameter of the sample disks are 1 cm. (b)

XRD patterns of the SnO₂-CF and Li-CF composites. SEM images of the (c, d) 3D CF framework, (e, f) porous SnO₂-CF composite, and (g, h) Li-CF composite with corresponding overlapped and individual elemental mapping images of Sn, O, and C.

5.1. Electrochemical performance of the Li-CF composite

To probe the cycling stability of the Li-CF composite, symmetric cells with two identical Li-CF electrodes were assembled using electrolyte with 1 M LiPF₆ in carbonate solvents and no additional additives. Bare Li foil symmetric cells served as the control. Figure 5.1.1 (a) – (b) display the extended voltage profiles of symmetric cells at 1 mA cm⁻² and 3 mA cm⁻² with 1 mAh cm⁻² capacity loading. At 1 mA cm⁻² (Figure 5.1.1 (a) and insets) and a higher current density of 3 mA cm⁻² (Figure 5.1.1. (b) and insets), the Li-CF electrodes exhibit stable and flat voltage profiles for 744 hours (372 cycles) and 120 hours (180 cycles), respectively. The results of rate performance tests of the Li-CF and bare Li symmetric cells starting at 0.5 mA cm⁻² and incrementing up to 5 mA cm⁻² are plotted in Figure S3 of the manuscript. Compared with bare Li foil, the voltage profile of the Li-CF electrode shows a lower overpotential. As previously reported by Pei et al, initial Li nuclei formation needs to overcome a higher energy barrier than steady growth of pre-existing nuclei.²²⁹ Large overpotentials and random voltage vibrations observed for the bare Li foil at the beginning of the initial discharge/charge curves can be ascribed to the irregular generation of Li dendritic seeds and severe SEI formation, marked as red circles in the insets of Figure 5.1.1. (a) – (b).²³⁰ In the following cycles, the Li foil symmetric cell shows a gradual increase in overpotential at both 1 mA cm⁻² and 3 mA cm⁻² current densities, which indicates uneven plating/stripping behavior with Li dendrites forming on the surface. The R_{ct} values for the bare Li foil and Li-CF electrodes is 117 Ω cm² and 36 Ω cm² after the 1st cycle, respectively, and decreases to 78 Ω cm² and 24 Ω cm² after 10 cycles. Compared with bare Li foil, the reduced interfacial resistance of the

Li-CF electrodes suggests better charge distribution and faster kinetics through the modified CF framework.

To better understand the electrochemical stability of the 3D framework, the morphologies of the bare Li foil and Li-CF electrodes were studied after 744 hours of cycling at 1 mA cm^{-2} . The illustration in Figure 5.1.1 (c) shows the layers of degradation in the planar Li foil after cycling and reveals the various failure mechanisms of conventional Li metal anodes. The bare Li foil in Figure 5.1.1 (d) gives fluctuated thickness vibrations with several isolated chunks of “dead” Li on the surface. The accumulated dead Li have detached from the bulk and denote the collapse of potential dendrites as well as the effects of excessive SEI formation.²³¹ Chunks of detached electroactive material are undesirable due to the inherent impact on cycling efficiency but they can also pose serious concerns to the electrode stability and safety. The lack of detached material in the Li-CF composite after 744 hours attests to the improved cycling with the 3D lithiophilic framework in Figure 5.1.1 (g). After washing away the dead Li, the exposed surface of the bare Li electrode exhibits pits and crevices, depicted in Figure 5.1.1 (e), which suggests that under the large volume variations of 1 mA cm^{-2} Li stripping/plating, the SEI layer cyclically breaks down and suffers from severe surface deformations. Evidence of persistent dendritic growth is also found underneath the layer of inactive dead Li at high magnifications, inset of Figure 5.1.1 (e) – (f). In combination with the various electrochemical measurements, the morphological results from SEM confirm that the infinite volume change, severe SEI, and Li dendrites were the three main issues that led to the failure of the working bare Li foils.

The uniform Li stripping/plating behavior of the lithiophilic Li-CF electrode contrasts strongly with the bare Li foil symmetric cell. Upon further examination, the design of the electrode is vindicated by the post-mortem cross-sectional and top view images, as seen in Figure 5.1.1 (g)

– (i). The CFs affords a stable and lithiophilic framework for homogeneous Li stripping/plating with a small volume expansion of 2.6 % (390 μm pristine thickness) as measured in Figure 5.1.1 (g). Notably, the porous structure is relatively impervious to the strain borne by planar structures that are incapable of accommodating the infinite volume change over long-term cycling durations. A high-magnification view in Figure 5.1.1 (i) shows the uniform and conformal re-adhesion of Li on the lithiophilic carbon framework, which is free of protruding dendritic growth after 744 hours cycling. The improved cycling stability and voltage hysteresis of the Li-CF electrodes can be attributed to three properties offered by the Li-CF framework: 1) the CF framework provides an electrically conductive highway to transport electrons; 2) the Li-Sn layer possesses a surface with improved wettability for Li ion deposition over long cycling durations; and 3) sufficient Li ion contact at the electrode/electrolyte interface enables homogeneous Li nucleation and uniform Li deposition at a minimized local current density. These properties of the Li-CF electrode help alleviate dendritic growth and offer a better technique to implement safe Li metal anodes.

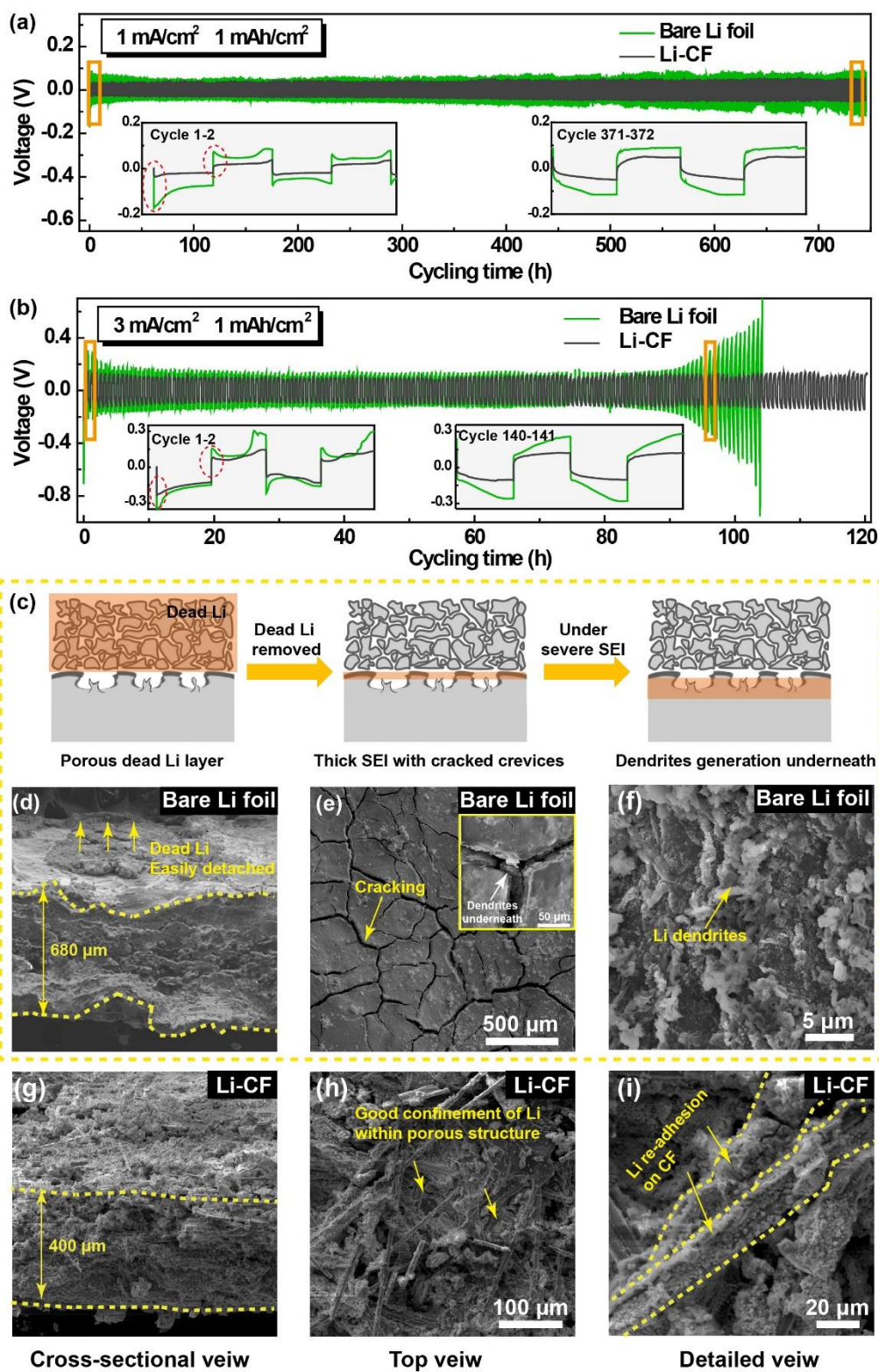


Figure 5.1.1. Electrochemical performance and morphology characterizations of bare Li foils and Li-CF electrodes. (a, b) Voltage profiles of bare Li symmetric cells (green) and Li-CF symmetric cells (black) at 1 mA cm^{-2} and 3 mA cm^{-2} current densities with a cycling capacity of 1 mAh cm^{-2} . (c) Graphical illustration of the multifaceted degradation in bare Li foils. (d - f) SEM image of the bare Li foil after cycling at 1 mA cm^{-2} , including (d) an overview of the Li foil covered in dead Li, (e) the cracked surface of the Li foil, washed clean of dead Li and (f) the dendritic morphology underneath. (g - i) SEM images of Li-CF electrodes after cycling at 1 mA cm^{-2} including a (g) cross-sectional image, (h) top view image of the Li-CF electrode, and a (i) zoomed-in SEM image showing the uniform re-adhesion of Li metal on Li-CF electrode after cycling 744 hours.

5.2. Failure mechanisms of lithium metal electrodes

The infinite volume change and dendrite growth are the leading catastrophic failure mechanisms of alkali metal batteries. To develop a better understanding of the different stripping/plating behavior in bare Li foil and Li-CF electrodes, symmetric cells were tested under galvanostatic stripping/plating with a capacity of 10 mAh cm^{-2} of Li at 1 mA cm^{-2} with ex situ SEM characterization. As previously reported by Dasgupta et al, the nucleation of new dendrites and initial surface pitting (caused by the detachment of dead Li) introduce an additional energy barrier, which gives rise to an increase in the cell overpotential at the end of the respective stripping/plating curve.²³⁰ This phenomenon is observed in the large voltage fluctuations of the stripping or plating curves for the Li foil symmetric cells in Figure 5.2.1 (a). Figure 5.2.1 (b) extrapolates the variation in theoretical thickness with areal capacity in which $48.5 \text{ }\mu\text{m}$ of bare Li metal foil results in 10 mAh cm^{-2} of capacity. The change in morphology of the bare Li metal electrode at different points while cycling is further investigated in Figure 5.2.1 (c) – (f). Initially, the thickness of the bare Li foil is $700 \text{ }\mu\text{m}$ and decreases to about $650 \text{ }\mu\text{m}$ after stripping 10 mAh

cm⁻² of Li. This is roughly in accordance with the calculation presented in Figure 5.2.1 (b) and suggests a large volume change during Li stripping. The zoomed-in top view SEM image in Figure 5.2.1 (e) exhibits a surface with surface pitting and discontinuities that are indicative of inhomogeneous Li stripping behavior. During the Li plating process, a non-uniform local electrical field distribution on the surface of an electrode amplifies the local deposition at critical points with the highest charge density. This line of reasoning leads to the dangerous dendritic behavior observed in Li metal anodes with a higher local current density in Figure 5.2.1 (f). After forming dendrites, newly generated SEI can electrically insulate thin dendritic structures and result in isolation followed by detachment from the bulk Li foil electrode, also known as “dead” Li (the inset in Figure 5.2.1 (f)). Excessive SEI formation also impedes charge transfer at the electrode/electrolyte interface and causes the overpotential to increase during plating.

The Li-CF symmetric cell, identified by the black line in Figure 5.2.1 (a), presents a smooth profile with a lower overpotential of 24 mV during the full stripping/plating cycle. The lithiophilic CF framework is generously accredited with the improved performance and is well preserved after Li thermal infusion with a thickness of 390 μm as shown in Figure 5.2.1 (g). After stripping 10 mAh cm⁻² of Li, the shape and thickness of the Li-CF electrode are well maintained, and a porous layer appears on the top side of the CF framework. Empty space between the fibers is observed in the porous layer with a total thickness of 130 μm (Figure 5.2.1 (h) – (i)). Unlike the bare Li foil, the coaxial structure of the Li-CF electrode is free of surface pitting after Li stripping (Figure 5.2.1j) and shows good re-adhesion of Li after plating (Figure 5.2.1 (k)). The bare Li foil and Li-CF electrodes were also tested at an ultrahigh current density of 10 mA cm⁻² with a capacity of 1 mAh cm⁻², the corresponding morphology of Li foil and Li-CF electrodes after 10 cycles are

displayed in Figure S11 of the manuscript. This result confirms the highly reversible nature of the modified metallic anodes on the 3D CF framework.

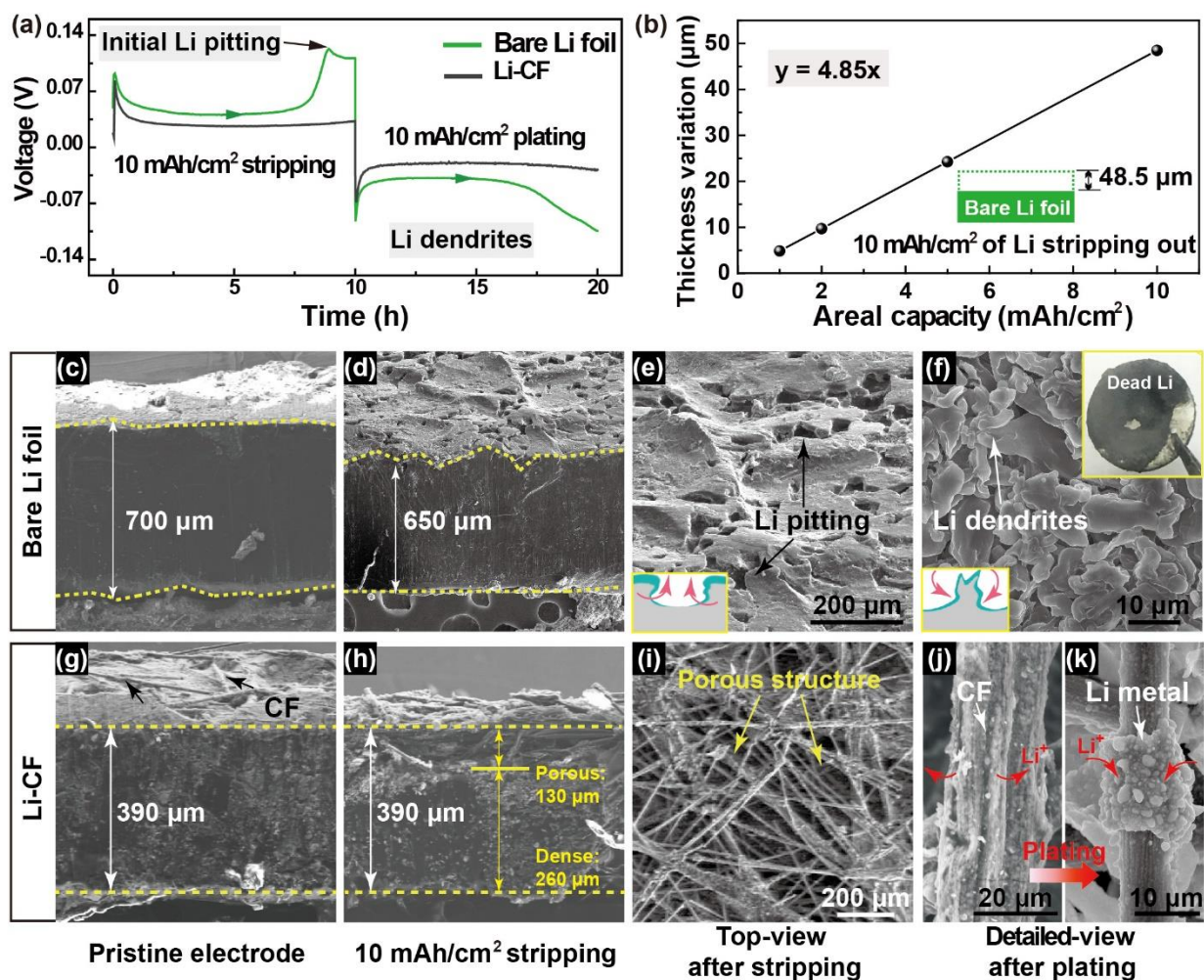


Figure 5.2.1. Morphological investigations of the bare Li foil and Li-CF electrodes at different stages while cycling. (a) Stripping/plating curves of cells using the bare Li foils (green) and Li-CF electrodes at 1 mA/cm² with a capacity of 10 mAh/cm². (b) Theoretical variation in thickness of the bare Li foil with areal capacity. (c, d) Cross-sectional view of the bare Li foil before and after stripping 10 mAh/cm² of Li with dramatic volume changes during the Li stripping process. (e) Top view of the bare Li foil after 10 mAh/cm² of stripping (e) and plating (f). Inset in (f) is the corresponding digital image of bare Li foil. (g, h) Cross-sectional view of the Li-CF electrodes

before and after stripping 10 mAh/cm² of Li, exhibiting a stable framework after Li stripping. (i) Top view of the Li-CF electrode after stripping 10 mAh/cm². (j, k) High-magnification images of the CF microscopic structure after 10 mAh/cm² of stripping (j) and plating (k).

5.3. Lithium Metal Host Full Cell Performance

To examine the stability and feasibility of Li-CF anodes in a practical battery system, full cells consisting of a Li-CF anode and LFP cathode (areal mass loading: 2.87 to 3.55 mg cm⁻²) were assembled and tested. Bare Li||LFP full cells are constructed as the control cells (Figure 5.3.1a). Figure 5.3.1b-d show the cycling performance of the Li-CF||LFP and bare Li||LFP full cells under a 2 C rate for 500 cycles. The Li-CF cells exhibit a 100.9 mAh g⁻¹ reversible capacity at 2 C rate with 90 % capacity retention and 99.7 % average efficiency after 500 cycles. The voltage hysteresis of the Li-CF cell slightly increases from 0.35 V to 0.48 V after the 1st and 500th cycle, respectively. In contrast, the bare Li cells display much faster capacity decay with 66 % retention and 96 % average efficiency after 500 cycles. An obvious oscillation in efficiency can also be observed during the last 100 cycles of the bare Li cells. This instability is compounded by the voltage hysteresis of the bare Li cell which increases from 0.64 V in the 1st cycle to 1.60 V in the 500th cycle. The stark contrast in the performance of the full cells at a high 2 C rate reveals the stability achieved by the Li-CF electrodes. Furthermore, compared with other 3D current collectors, the Li-CF electrode with improved wettability can act as a reservoir to pre-store Li and offset Li loss during repeated cycling, thus enabling a higher retention when paired with low efficiency and energy dense positive electrodes.

Full cells with the Li-CF electrode are projected to achieve a higher gravimetric energy density at a lower cost than commercial graphite electrodes due to the dendrite-free Li metal design (Figure 4.2.1e). Notably, the energy densities are calculated based on the total mass of the positive

and negative materials.²³² Full cells with LFP||Li-CF demonstrate a high energy density of 489 Wh kg⁻¹, close to pure Li foil full cells (522 Wh kg⁻¹), and surpassing graphite-based full cells (369 Wh kg⁻¹) by 33 %. This dendrite-free Li metal design concept can also be applied to other novel high-energy-density Li-ion based batteries technology beyond LFP-based full cells due to the facial manufacturing processes including solution-based methods and molten Li infusion.

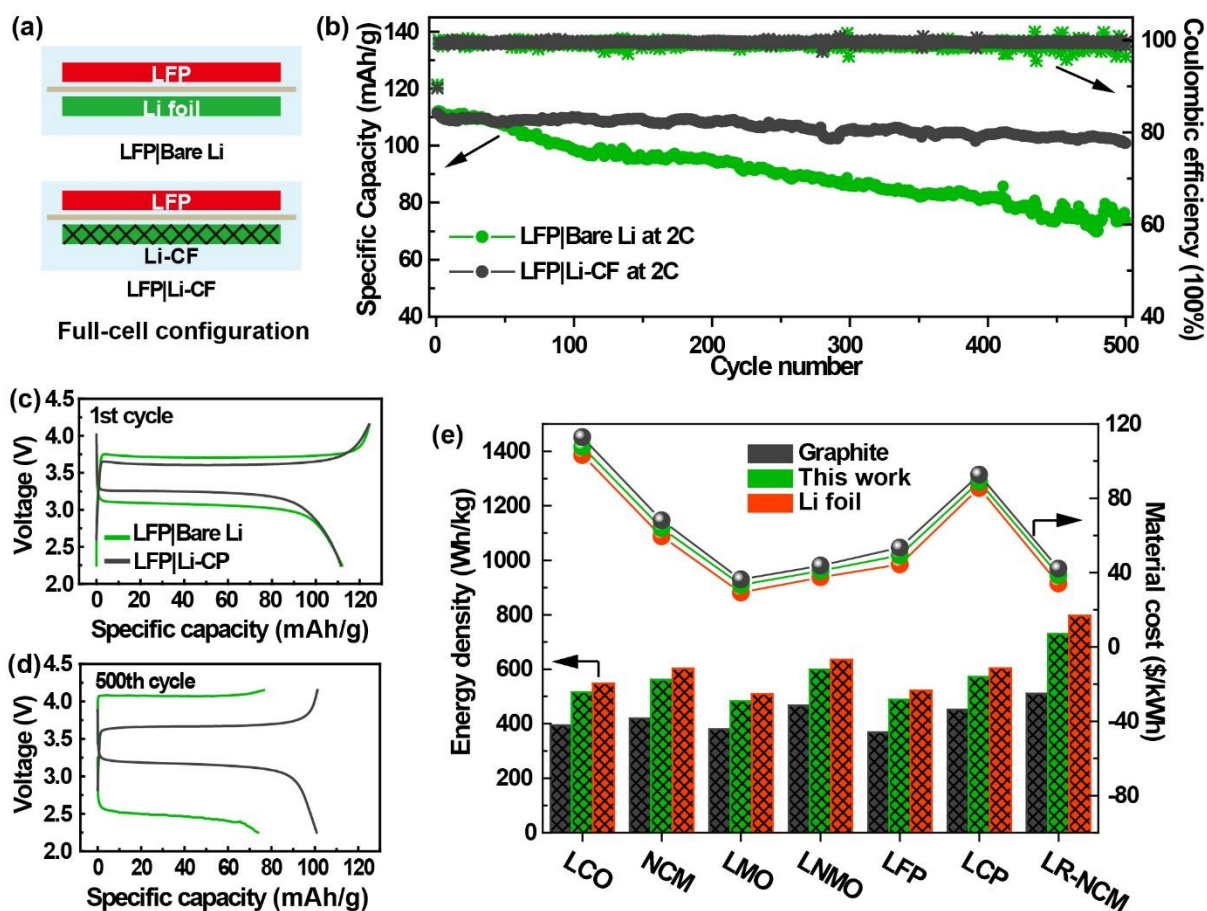


Figure 5.3.1. Electrochemical performance of Li-CF||LiFePO₄ full cells. (a) Graphical illustration of full-cell configuration using bare Li foil and Li-CF anodes. (b) Long-term cycling performance of Li-CF||LiFePO₄ (black) and bare Li||LiFePO₄ (green) full cells at 2 C for 500 cycles. (c-d) Corresponding voltage profiles comparison of Li-CF||LiFePO₄ and bare Li||LiFePO₄ cells for 1st,

and 500th cycle. (e) Energy density and cost analysis of Li batteries with Li-CF electrodes (green), Li foil (orange), and graphite (black) paired with typical cathode materials.²³³

5.4. Energy Storage Materials from High Temperature Joule Heating

Fast carbothermal shock (CTS) induces a high temperature environment that can reach up to 3,000 K for carbon based materials with a ramping rate of 20,000 K sec⁻¹, as determined by the applied electric field and resistivity of the sample. Implementation of the CTS process requires an inert atmosphere as well as the initial structural integrity and electric resistivity of the substrate. Aside from these requirements, any conductive carbonaceous material can be heated by direct ohmic heating and many more materials can be subjected to indirect radiative heating. Under short timespans and at high temperatures, the Hu group has reported numerous synthesis mechanisms that can be uniquely achieved by the CTS process including carbon welding, amorphization, alloying, and controlled re-nucleation.^{71,73,234} Two new mechanisms are reported, namely, the thermal decomposition of salt precursor in a carbon matrix for fast synthesis of coated nanoparticles and the fast exfoliation of carbon nanofibers.

The CTS process is performed with a Keithley 2425 SourceMeter using KickStart instrument control software in an argon filled glovebox (O₂ level < 0.1 ppm and H₂O level < 0.1 ppm). Set temperatures are achieved according to the Joule-Lenz law and light emitted from the specimens is best represented by grey body approximations to determine the corresponding temperature (Equation 5.4.1, below):

$$B_{\lambda}(\lambda, T) = \gamma \varepsilon \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1} \quad (5.4.1)$$

where h is Planck's constant, c is the speed of light, λ is the wavelength of light, k_B is Boltzmann's constant, and γ is a scaling constant introduced for fitting. Figure 5.4.1 (a) plots the voltage across the sample as a function of the driving current while the inset depicts the experimental setup, including spectrum acquisition. A 30 μ m optical fiber was used to collect the emitted spectrum for

temperature calculations. The emissivity of specimens in this work are assumed to be similar to carbon, approximately 0.8.

In these experiments, CTS of precursor-imbedded electrospun mats is performed to enable dynamic diffusion of tin through the carbon matrix. Tin chloride (SnCl_2) salt is selected as the metal source (melting point of Sn is 232 °C) due to its cost, ability to dissolve in polar dimethylformamide (DMF), and improved performance as a nanostructured negative electrode. Careful control of the CTS parameters results in fine tuning of the resultant tin particle growth and distribution on the nanofiber mat. The salt precursor thermally decomposes into liquid phase tin which diffuses rapidly to defect sites on the fiber surface and simultaneously emits chlorine gas. Under short timescales, nanoscale wetting and particle coalescence can lead to formation of uniform globular nanoparticles with applications in batteries and other prospective electrochemical devices. The growth of NPs out of the carbon nanofiber network is characterized by *ex situ* measurements.

To prepare the fibers, polyacrylonitrile (PAN) is dissolved in DMF to form an 8 wt% solution, followed by the addition of tin chloride salt precursor. The effect of inorganic salt precursor on electrospinning PAN polymer solutions is well reported in the literature.^{235–237} In general, salt concentration directly impacts the viscosity and conductivity of the solution such that the fiber diameter increases, shearing strength decreases, and conductance increases.²³⁸ We observe beadless and uniform nanofibers with few shape deformities by electrospinning the polymer solution at a voltage of 15 kV, a feed rate of approximately 1 mL hr⁻¹, and a distance of 10 cm. The resultant CNF- SnCl_2 fibers are collected from the rotating drum and stabilized at 573 K for 5 hours in air, and then at 873 K for 2 hours in argon. Samples for CTS are assembled with

silver paste on conductive electrode contacts and suspended on glass are shown in the inset of Figure 5.4.2 (a).

In contrast to a pure resistor, whose voltage linearly increases with current, the potential across the CNF-SnCl₂ sample drops as the material is carbonized during the CTS process as seen in Figure 5.4.1 (a). This drop in potential is indicative of a change in conductivity that we measured under a small ± 10 mV sweep before and after the CTS process, as shown in Figure 5.4.1 (b). As the crystallinity of CNF increases and defects are removed, the resistivity of the CNF-SnCl₂ mat drops drastically by a factor of 7262 from a 2 W input power (Figure 5.4.1 (b)). Figure 6.1.2c shows how spectral irradiance scales with increasing power between 360 to 950 nm. The fitted temperature as a function of input power is given in Figure 6.1.1d and remains nearly linear in the measured range.

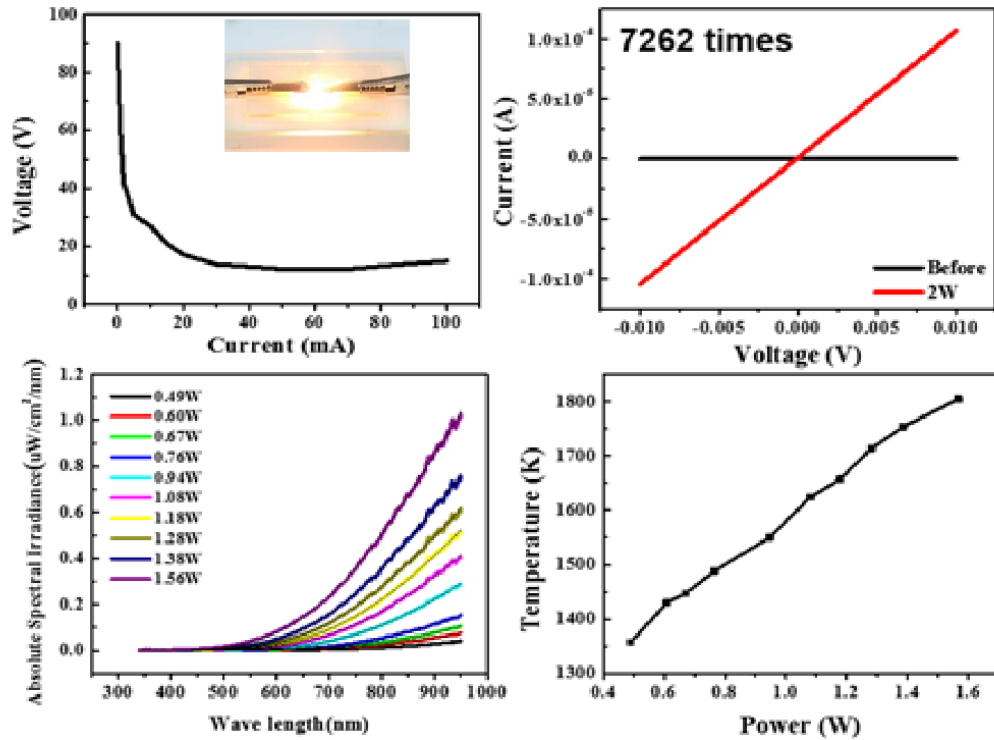


Figure 5.4.1. Fast annealing process and characterizations. (a) Current vs. voltage profile of CNF-SnCl₂ during the CTS process. The inset shows the experimental setup for the CTS process and

spectrum collection. (b) Resistance measurement for CNF-SnCl₂ before (black) and after (red) Joule heating at 2 W. (c) Collected spectra and (d) fitted temperature of CNF-SnCl₂ by Joule heating.

The morphology and structure of the materials in these preliminary works were characterized using a Hitachi SU-70 field emission scanning electron microscope (SEM) with energy dispersive v-ray spectroscopy (EDS), a Thermo Nicolet NEXUS 670 Fourier-transform infrared spectrometer (FTIR) ranging from 600 to 4000 cm⁻¹ under attenuated total reflection (ATR) mode, and a D8 Advance x-ray diffraction (XRD) system with Cu K α radiation ($\lambda = 1.5406$ Å). The transmission electron microscopy results were collected with help from colleagues using a JEOL 2100F field-emission TEM. Before conducting x-ray diffraction of the air sensitive samples, electrodes are sealed in Kapton tape (DuPont Inc.) in a glovebox.

The fast quenching of the system after CTS ensures the spherical Sn nanoparticles maintain their unique morphology and poor wetting over longer timescales on the CNF matrix (Figure 5.4.2 (a – b)). A thin dual amorphous and crystalline carbon shell (< 10 nm) was found on the Sn NPs, anchoring them onto the CNF matrix (Figure 6.1.2d). The size distribution of the Sn NPs is controlled by sweeping the current over time. Under long timescales, the large particles wet poorly on the carbon matrix, with ripening of the particles scaling faster than heterogeneous nucleation on new defect sites. This is confirmed by the general lack of new small NPs on the CNF matrix under longer heating timescales. After partitioning the Sn-CNF matrix, uniform mats will be assembled into coin cells for galvanostatic cycling and further electrochemical characterization. Future work will need to improve the consistency and uniformity of the Sn-CNF matrix for more stable electrochemical performance.

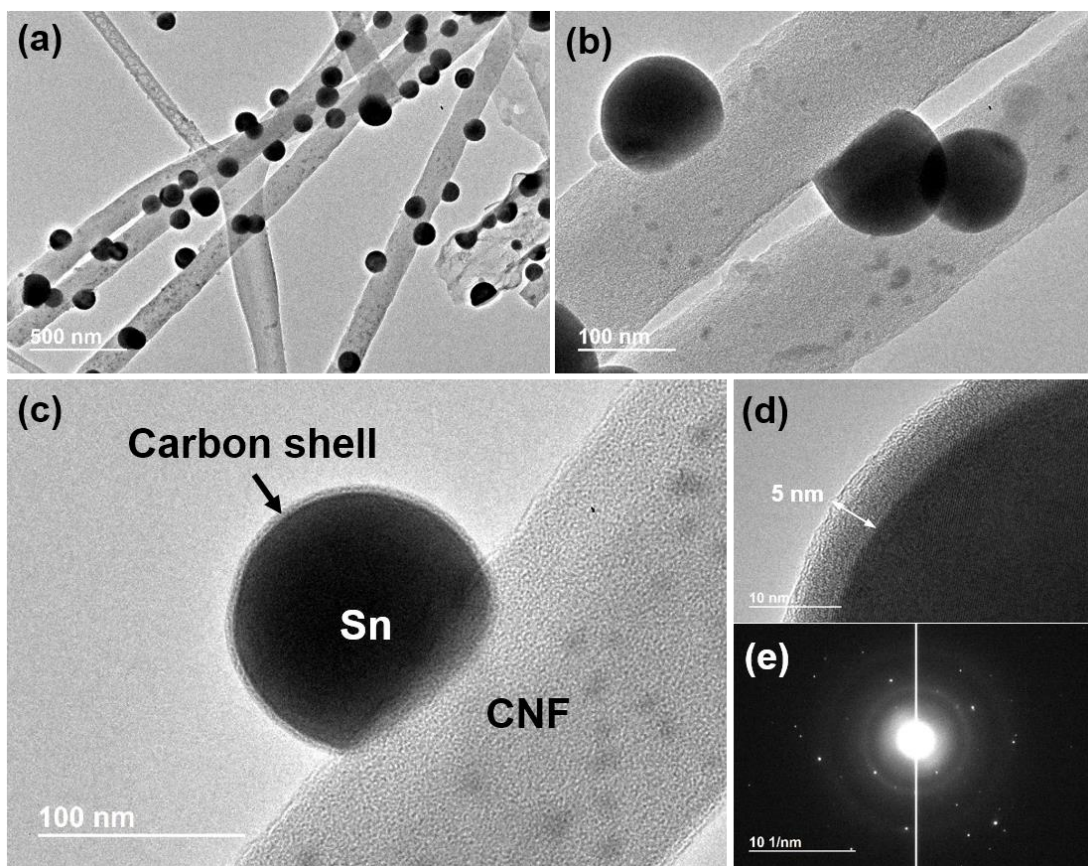


Figure 5.4.2. Sample TEM images of the Sn-CNF carbon host for alkali metal electrodes. (a-d) TEM images of the Sn-CNF composite after the Joule heating process show uniformly distributed Sn nanoparticles with a diameter of approximately 100 nm. A 5 nm dual amorphous and crystalline carbon shell was also found on each nanoparticle. (e) The electron diffraction pattern of the Sn nanoparticles on CNF.

To date, the synthesis of hollow graphitic carbon nanofibers (HGCNFs) depends on vapor deposition processes, catalytically induced formation mechanisms, and high temperature thermal annealing. Despite the high capital costs and complexity of these techniques, HGCNFs are highly sought for a variety of current and prospective electrochemical applications as conductive additives and hosts. In this study, the ultrafast exfoliation of HGCNFs by CTS of electrospun polyacrylonitrile (PAN) fibers is reported. The novel formation of HGCNF is investigated by tuning the heating rate between 5 and 10^4 K min⁻¹. Under a 10^4 K min⁻¹ heating rate, an 800% increase in fiber diameter is achieved concurrently with the release of thermal decomposition products. Characterization by scanning electron microscopy, Raman, X-ray diffraction, high-resolution transmission electron microscopy, x-ray photoelectron spectroscopy, and I-V tests indicate the control and appeal of the facile process. Application of the HGCNFs for Li-ion redox reactions is also being investigated to confirm the ease and applicability of Joule heated HGCNFs for more complex nanostructures.

CNF films were obtained by electrospinning PAN in DMF (8 wt.%) followed by thermal stabilization at 260 °C and carbonization at 600 °C. PAN-derived CNF was selected because of its simple molecular structure, easiness to form nanofibers by electrospinning, and the resultant high quality CNFs. The electrospun PAN fibers are collected in a rotational drum to ensure sample uniformity in thickness and density. After the brief pretreatment, the CNF samples were connected to copper electrodes with silver paste and suspended on a glass substrate to avoid befouling interfaces under high temperatures. When a more rapid heating rate (10^4 K min⁻¹) is applied, the diameter of the CNF expands and hollow fibers are created as shown from preliminary work in Figure 5.4.3. The electrospun fibers are dense and briefly stabilized at a low temperature to ensure a high defect concentration before CTS. The CTS process was performed on CNF films (4 mm

length, 2 mm width, 30 μm thickness) with a driving current between 0.1 mA to 1 A (Figure 6.2.1b). Further morphological and electrochemical characterization of the exfoliated fibers is necessary. Symmetric cell configurations are be employed to probe the Li stripping/plating behavior of lithium metal host electrodes in 2032-type coin cells. The performance of the symmetric cells is still being tuned by colleagues through the development of the electrolyte system.

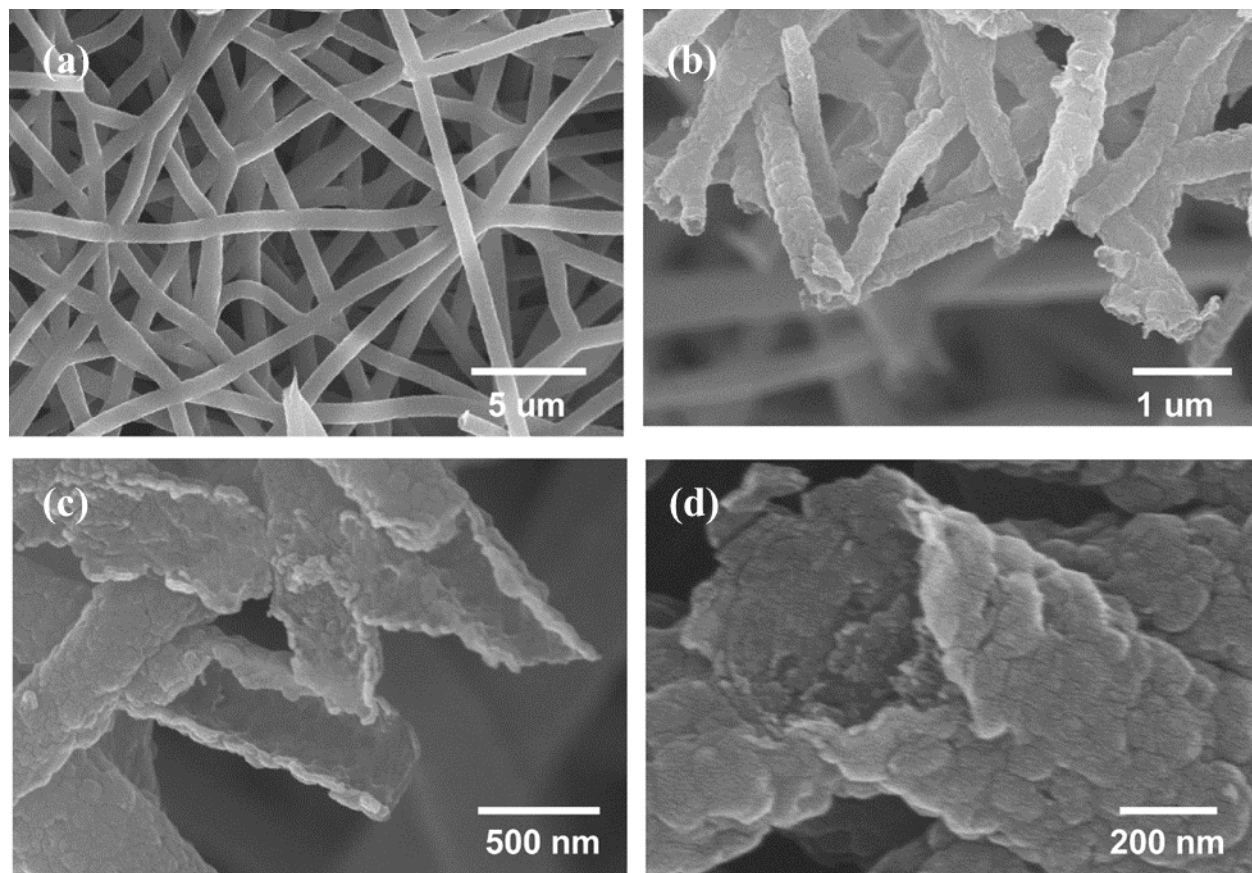


Figure 5.4.3. (a-d) SEM images of the exfoliated carbon nanofibers after the CTS process at varying magnifications.

Chapter 6: Conclusions and Perspectives

In this dissertation, experiments from three maturing fields of lithium ion battery research are reported. The discussion below briefly summarizes the conclusions from each work.

Chapter 3 details experiments pertaining to composite silicon negative electrodes as well as additional high-mass loading or flexible electrodes for high-energy full cells. Section 3.1 outlines the preparation of functionalized and coated silicon nanoparticles for high energy density lithium ion batteries. A provisional patent was submitted to protect and encompass the innovations from this research. The synthesis omits all high temperature annealing steps and chemical etching processing. The silicon particles are functionalized with amine groups in solution, and concurrently, graphene oxide is partially chemically reduced in a dilute acid. The morphology of the Si additive and the additive in composite negative electrodes is discussed in Section 3.2. The RGO and binder are thoroughly mixed in the composite electrode such that the functionalized additive disperses as a thin layer on the graphite particles. Section 3.3 reports that half-cell configurations of the Si composite negative electrode outperform composite electrodes with similar Si content. The most apparent improvement in performance comes from the increased efficiency of the functionalized Si additive during the first 5 cycles without prelithiation additives or procedures. The ICE of the negative electrodes improves from 90 to 92 %, and in subsequent cycles, the efficiency of the functionalized negative electrode jumps up to 99 %. In Section 3.4, the solution-based approach for functionalized Si composite electrodes is applied to high mass loading and binder-less electrodes. A separate study published in *Advanced Energy Materials* on conductive nanofiber networks for thick and energy dense phosphate-based positive electrodes is also briefly described. Thorough experiments detailed in Section 3.5 investigate the ideal voltage window for balancing the retention and energy density of Composite Si||NMC full cells. Given the

finite amount of Li in full cell configurations, this work shows that avoiding the phase transition of silicon at 3.25 V in cell configurations with NMC532 greatly improves retention, albeit while sacrificing the volumetric energy density by 15 - 30 %. In Section 3.6, the weight ratio of PAA and SBR aqueous binder is varied in binary blended mixtures and thin film measurements of strength and swelling are conducted. The performance of the PAA60:SBR40 blend resembles a hard and tough polymer with the advantages of the brittle PAA and elastomeric SBR components. In the last section of Chapter 3, the performance of ultrathin and flexible LFP||Gr full cells is given for the emerging wearable and internet-of-things markets. The prototypes retain 80.0% of their capacity at a 2C rate after 430 cycles and 78.6% after 1000 cycles.

In Chapter 4, three systems are presented to replace the flammable, carbonate-based electrolyte which is the industry standard for energy-dense lithium ion batteries. Section 4.1 details the design and implementation of a novel, mixed ionic liquid (MIL) consisting of PYR13TFSI:ethylene carbonate:diethyl carbonate:vinylene carbonate (40:29:29:2 vol%) with 0.58 M LiPF₆ and 0.15 M LiBOB for phase I of the flexible battery project. Of the three components, the ionic liquid continuously decomposes to form SEI during lithiation of the Si composite electrode. This mechanism overwhelmingly contributes to irreversible capacity loss in the full cell and, as a result, this approach was abandoned. In Section 4.2, a pure sulfolane system is investigated for layered 532NMC||Gr full cells. Wetting of the electrodes in coin cells is improved by thermally activating the cells at 60 °C for 1 – 2 hours before cycling and two systems of varying concentration are tested, but perform poorly without additional viscous co-solvents. Therefore the sulfone system has been postponed for the “High-Energy Density, Long Cycle Life and Safe Lithium Ion Batteries” project, with Analog Devices Incorporated. Section 4.3 describes the characterization of two fluorinated-based systems, 1 m LiPF₆ in HFE:FEC:FEMC and

HFE:FEC:DMC (2:2:6), which show great promise for energy-dense and flame-retardant full cells. However, while the HFE:FEC:FEMC system retains 80 % of its capacity for only 30 cycles at C/5, the HFE:FEC:DMC system retains the same amount of capacity for 60 cycles, with an initial energy density 600 Wh L⁻¹. Therefore, after rigorous electrochemical and flammability testing, the fluorinated system with DMC is adopted for NMC532||Si composite full cells. The performance and characterization of the additives in Section 4.4 lead to a number of surprising conclusions regarding the ideal interfacial properties and species for NMC||SiGr full cell configurations. The pyrocarbonate additive, DEPC, forms a stable SEI in a carbonate system for 60 cycles but then decays quickly, afterwards. Furthermore, the electrolyte does not store well with DEPC and may cause acute corrosion of the polymer separator and other battery components. Lithium nitrate performed much better in full cell configurations with an average coulombic efficiency of 99.63 % in the first 100 cycles at C/5, significantly higher than any previously tested additive package. At C/5, the cell also retains 80 % of its capacity for 100 cycles between 4.3 – 3.0 V. It would be worthwhile to test this additive in the flame-retardant, fluorinated system both with and without LiDFOB. LiDFOB was tested to great success in the fluorinated electrolyte system. Impedance and storage tests indicate a stable SEI was formed on the Si composite electrode. Further characterization by SEM and EDS indicate that a more oxygen-rich and polymeric SEI forms on the electrode which explains the strong electrochemical performance. An additive package consisting of 2 to 3 wt% LiDFOB in the fluorinated electrolyte achieves the highest energy output for the NMC532||SiGr system with 741 to 774 Wh L⁻¹ volumetric energy density and between 99.3 to 99.4 % average coulombic efficiency, respectively.

Chapter 5 includes novel electrode designs and methods for synthesizing high-capacity Li metal electrodes. Section 5.1 describes the stable and dendrite-free alkali metal electrodes made

by thermally pre-loading molten Li or Na into a three-dimensional (3D) framework with high alkali wettability. This work was published in *Advanced Energy Materials* with co-first authors Dr. Zhang and Dr. Wang. The most critical failure mechanisms of metallic Li anodes are thoroughly examined via *ex-situ* SEM and described in Section 5.2 while Section 5.3 reports on full cells with Li-CF||LFP electrodes. Section 5.4 describes the synthesis of unique HGCNF and Sn-CNF hosts by the carbothermal shock method. The challenges associated with these two projects pertain to (i) controlling the ultrafast synthesis of the carbon frameworks by CTS and (ii) ensuring the architectures are homogeneous and repeatable. These issues are managed by careful control of the processing parameters and morphology of the precursor materials. The high temperature environment induced by the ultrafast carbothermal shock method provides an interesting platform for developing novel energy storage materials.

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