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Design and Evaluation of Three Dimensional (3D) Current Collectors for Lithium Metal Batteries: Insights from Meta-Analysis and Experimental Studies

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Abstract

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Batteries: Insights from Meta-Analysis and Experimental Studies

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As energy demand for mobile applications grows exponentially worldwide, energy storage solutions are becoming increasingly important. Electrochemical storage in the form of batteries is already widespread, but design demands for new applications require novel solutions. Lithium metal batteries (LMBs) are regarded as a promising avenue for significantly boosting the gravimetric energy density of batteries, a property that is particularly important for electric vehicles. However, the instability of the lithium metal anode (LMA) continues to hinder performance. Three-dimensional (3D) current collectors (electrically conductive substrates) have frequently been proposed as a solution, but many questions remain regarding which properties are most critical for performance and how the structures behave in realistic configurations. This thesis addresses these questions to guide the design and implementation of 3D current collectors in high-energy-density LMBs.

A vast body of literature already exists surrounding 3D current collectors for LMA. However, few efforts have systematically analyzed the relationships between structural parameters

of the current collector and anode performance to inform design. A coupled meta-analysis of published results and machine learning (ML) and data science techniques was undertaken to extract trends between 3D current collector structure and composition and cell performance metrics of Coulombic efficiency (CE) and cycle life (number of charge-discharge cycles before failure). The analysis revealed no correlation between structural pore diameter and performance but showed that a low to moderate specific surface area correlates to higher CE and cycle life than high specific surfaces areas. The analysis also indicated that the presence of oxygen and tin on base structures improves performance. These findings were validated experimentally: a low specific surface area carbon current collector outperformed a high surface area counterpart, and 3D copper structures incorporating oxygen and tin outperformed unmodified structures. The study highlights the value of meta-analysis for uncovering cross-cutting insights across diverse studies.

Beyond the lack of clarity on optimal structural properties, few studies have examined the effects of combining 3D current collectors with various electrolytes (ionic conductor between electrodes) or have incorporated a lithium reservoir. Four commercially available copper current collectors were paired with four different electrolytes to assess how these factors influence cycling performance with a 4 mAh/cm² lithium reservoir. Coulombic efficiency (CE) measurements revealed no statistically significant difference in CE across different current collectors within the same electrolyte. However, significant variation was observed when the electrolyte was changed while using the same current collector. Although polarization, electrochemical impedance, and lithium morphology varied between structures and electrolytes, no consistent patterns emerged to identify a clearly superior current collector structure. These results suggest that when a lithium reservoir is used, the choice of current collector structure becomes less critical, and efforts should instead prioritize electrolyte selection and design.

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DEDICATION

This work is dedicated to the family and friends who stayed by my side and offered so much support and encouragement through the roller coaster that is a PhD program.

To my family: my mom Kate, and my sisters Mary Ann and Christine, the best cheerleaders and the most resilient, powerful, and caring women I know.

To my friends, particularly the ice cream and cheeky pint squad and my climbing crew: thank you for being listening ears, a safe space, and an escape.

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Chapter 1. Introduction

1.1. MOTIVATION

The world is rapidly electrifying. In the past sixty years, global electricity production has increased five-fold.¹ Electricity has become an integral aspect of our lives, providing basic necessities such as lighting, heating, cooking and food preservation, and entertainment. Population growth as well as the electrification and increased scale of industrial processes have contributed to exponential growth. Expanded use of portable electrical devices, from the scale of cell phones up to passenger transportation, has also driven demand. Even more recently, in the last ten years, rapid growth of cloud storage, computing, and AI are putting even greater pressure on electricity generation.

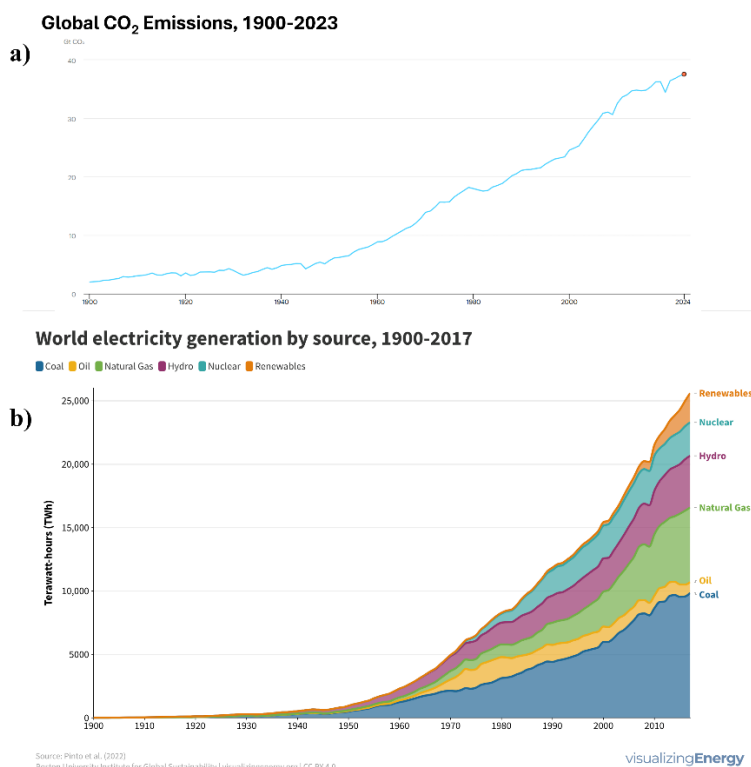


Figure 1-1: Global CO₂ emissions (a) and electricity generation (b) have both risen rapidly in the last 60-70 years.¹⁻³

The growth of energy production has corresponded to the rise in global emissions due to the prevalence of the use of fossil fuels to create electricity (Fig. 1-1) ¹⁻³. According to the United States Energy Information Administration, electricity production in the U.S. primarily uses fossil fuels (coal, natural gas, and petroleum), nuclear power, and renewable energy sources. In response to concerns and activism from the scientific community, production shifted in the mid-1980s away from coal towards natural gas to reduce emissions. More recently, in the last 20 years, renewable energy generation has greatly increased, producing electricity with no emissions output at generation.

While consumption and production frequently dominate discussion of energy usage, storage is also a critical pillar of the electricity ecosystem on which our world currently relies. Relating to production, many forms of renewable generation, including the two most prevalent of solar and wind generation, are limited in application due to the intermittent nature of the generation. Energy storage greatly increases the percentage of renewably generated electricity that can be utilized. Around consumption, electrochemical energy storage in the form of batteries has revolutionized how the average person uses electrical devices. Portable electronic device use and ownership has exponentially increased since the commercialization of rechargeable lithium-ion batteries by Sony Inc. in 1991. Today, batteries are ubiquitous, freeing users from the physical constraints of a wired electrical connection.

While batteries are commonplace in today's world, there are still many applications in which current battery technology is insufficient. Large-scale storage for grid-scale renewable generation plants has yet to be optimized or widely commercialized. Electrical vehicles (EVs) have grown in popularity as well, with over 20% of new light-duty vehicle sales in September of 2024 consisting of fully electric, hybrid, or plug-in hybrid vehicles according to the U.S. Energy

Information Administration. Though already on the market, manufacturers continue to strive to improve EVs to better compete with internal combustion engine vehicles, including improving battery performance. Namely, battery capacity currently limits EV range to less than that of internal combustion vehicles, and concerns over the longevity and safety of batteries still affect demand. This research aims to accelerate battery development and drive advances for energy storage in EVs.

1.2. BATTERIES: OVERVIEW OF ELECTROCHEMICAL ENERGY STORAGE

1.2.1. Battery Anatomy and Operation

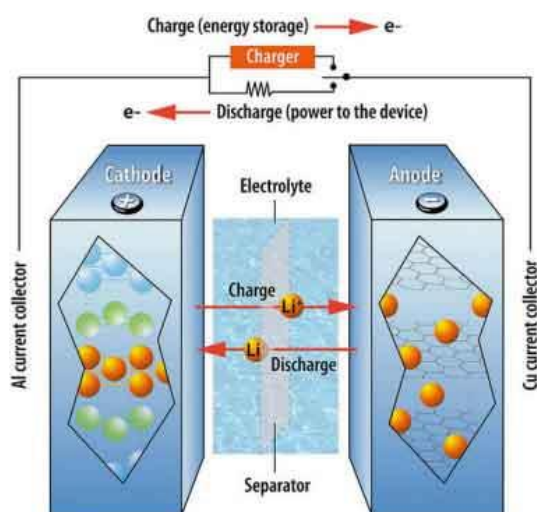


Figure 1-2: Schematic of a lithium-ion battery in operation.⁵

Batteries are frequently perceived as incomprehensible black boxes, but their operating principles are surprisingly straightforward. A battery primarily consists of four components: a cathode (positive electrode), an anode (negative electrode), an electrolyte, and an external electrically conductive path (Fig. 1-2). Ions move between the electrodes through the electrolyte while electrons flow via the external path. A separator, immersed in the electrolyte and positioned between the electrodes prevents electrical contact in compact cell configurations. The electrodes

are fabricated on a thin layer of metal, known as the current collector, which forms part of the external conductive path.

The difference in potential between the positive and negative electrodes defines the voltage of a battery and serves as the driving force for its operation. When the potential difference is sufficiently large, the charge-carrying ion is spontaneously oxidized at the negative electrode and reduced at the positive electrode. The movement of electrons through the external circuit to balance the charge during these reactions generates the current that powers devices. As ions are exchanged, the potential difference decreases, causing the voltage to drop until the reaction can no longer proceed spontaneously. At this stage, a primary (non-rechargeable) battery is considered “dead,” fully drained of energy and unable to accept more. In contrast, the reaction can be reversed in a secondary (rechargeable) battery by applying electrical energy to the cell. A current is applied in the opposite direction, driving electrons from the positive electrode to the negative electrode. The process causes oxidation of the ion at the positive electrode and reduction at the negative electrode. The battery is charged in this way until the voltage increases to a level where the reaction can proceed spontaneously again. Only certain combinations of materials enable the reaction to occur reversibly, and among these, secondary lithium-ion batteries are the most widely known and utilized.

Lithium-ion batteries (LIBs), as their name suggests, utilize lithium ions to move charge between electrodes. Lithium is exceptionally light, making it ideal for applications in which weight is a critical factor. Its small ionic radius allows it to fit into various materials more easily, and its low potential compared to most other materials increases the battery operating voltage, allowing higher power output. Most LIBs on the market today use a lithiated transition metal oxide or phosphate cathode, such as lithium nickel-manganese-cobalt oxide (NMC) or lithium iron

phosphate (LFP), coated on aluminum foil. The anodes are typically made of graphite on copper foil, while the electrolytes consist of lithium salts dissolved in organic solvents. This cell design has been extensively optimized, delivering high efficiency and long cycle life.

Three common battery arrangements are employed in research. Full cells are batteries in which the two electrodes produce a high enough voltage and wide enough voltage range for practical applications. One example is the NMC|graphite LIB described above. Both electrodes have limited capacity, or how much of the charge-carrying ion they can hold. Half-cells are used to isolate one electrode for study and consist of one designated limited electrode counter a large reservoir of the charge-carrying ion. A graphite|lithium cell is one such example. Finally, symmetric cells may also be employed, typically to study electrolyte. Symmetric cells place a material against itself. A common arrangement found in literature is lithium|lithium cells. Each cell type is preferred for studying different properties of the cell's components.

1.2.2. Common Performance Metrics

When evaluating battery performance, a wide variety of metrics are utilized depending on application. Within this work, performance is measured in two ways: Coulombic efficiency and cycle life. A brief description is provided here, and additional details particular to experimentation are provided in the relevant chapter.

Coulombic efficiency (CE) is commonly used to estimate the efficiency of lithium movement from one electrode to another and back. This efficiency is frequently used to roughly estimate the lifetime of the battery and can provide an indication of battery health. Sudden changes in CE between cycles can signal imminent cell death or perturbations in the battery. As implied by the name, CE is calculated based on the current passed during charge and discharge during a

single cycle. The current passed is converted to capacity based on the time of each half cycle, and CE calculated as:

$$CE (\%) = \frac{\text{Discharge Capacity}}{\text{Charge Capacity}} * 100 \quad \text{Eq. 1-1}$$

CE is determined by the limited electrode, where the percent CE represents how many of the charge-carrying ions traveled from the limiting electrode and then returned. Charge and discharge must be designated with this frame of reference. In full cells, it is a simple matter as full cell design sets the cathode as the limiting electrode. In discharge, ions leave the cathode and reduce at the anode, and in charge, the ions return and are reduced at the cathode. In half-cells, particular attention must be paid to ensure that the limiting electrode is the point of measurement.

CE as a measure of efficiency, while widespread and the most straightforward measurement, has inherent issues.⁶ As stated, the current passed between electrodes is used to calculate CE, and an assumption is made that every electron that composes that current goes towards oxidizing and reducing the charge-carrying ion. In some systems, this is a reasonable assumption, but side reactions are more prevalent in certain chemistries than others. These electrochemical reactions consume electrons to create byproducts that are not electrochemically reversible. CE measurements cannot differentiate between the primary electrochemical reaction involving the charge-carrying ion and side reactions. Despite this shortfall, CE is a trusted metric employed in both half-cell and full-cell testing. Details of the experimental determination of CE specific to this work are included in each experimental chapter.

Cycle life is the second key performance metric frequently reported and utilized in this work. At its most basic definition, cycle life is the number of cycles a battery cell can achieve before cell death. The definition of cell death is not static, however. In some cases, particularly half- and symmetric cells, cell death is the shorting of a cell. For full cells, cell death or end of life

is typically defined by the discharge capacity dropping to a set percentage of its original value. In many consumer devices and EVs, batteries are considered to have reached end of life when their capacity dropped to 80% of the initial capacity. It is important to note in literature what the definition of end of life is set as, particularly when comparing performance.

1.2.3. Energy Density

Beyond standard performance metrics, there are other properties of batteries that are critical to performance in different applications. For EVs and other weight sensitive applications, one of the most critical metrics is energy density. Energy density is measured in two ways: gravimetrically (energy per mass) and volumetrically (energy per volume). For EVs, both metrics are important, though the focus is often on gravimetric energy density. To enable longer ranges on a single charge and effectively compete with internal combustion engine vehicles, EV batteries need to be lightweight while storing significant amounts of energy. The commercialization of LIBs was revolutionary in part because their energy density was much higher than other commercial battery chemistries. That energy density has been optimized in the last 30 years. While sufficient for many applications, the demand for EVs that compete with internal combustion engine vehicles, as well as a push for other battery-powered transportation, requires even greater energy density than can currently be achieved. LIBs have hit a ceiling in energy density that seems unlikely to be surpassed with the current design paradigm, limiting EVs to ranges less than that of internal combustion vehicles. Innovative, out-of-the-box approaches will be essential to achieving further improvement and improve users' experiences by reducing range anxiety and allowing further travel on a single charge.

1.3. LITHIUM METAL BATTERIES FOR HIGH ENERGY DENSITY

1.3.1. Benefits

One of the most promising methods to dramatically improve energy density is to replace the graphite anode in LIBs with pure lithium metal, giving rise to a new class of batteries known as lithium metal batteries (LMBs). Lithium's extremely low molar mass and a high theoretical energy density - providing 3860 mAh/g compared to graphite's capacity of 372 mAh/g - make it a superior alternative. The significant difference means that much less lithium is required than graphite, leading to thinner anodes and greater volumetric energy density. Additionally, lithium's low potential of -3.04V vs the standard hydrogen electrode (compared to graphite's potential of -2.84V) expands the voltage window within which the cell can operate, allowing more energy to be extracted.⁷ Together, the reduction in anode mass and the expanded voltage window can more than double the gravimetric energy density of LMBs compared to LIBs (Fig. 1-3).^{8,9}

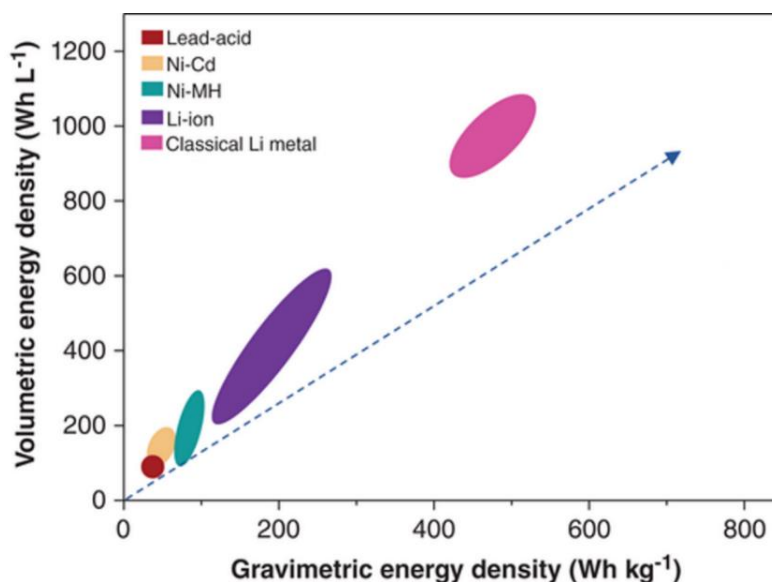


Figure 1-3: Energy density of common battery chemistries, demonstrating the high volumetric and gravimetric energy density of lithium metal batteries compared to lithium-ion.⁹

1.3.2. Challenges

Despite the benefits of using pure lithium metal as an anode material, there are many challenges to its practical application. The low potential that makes lithium so attractive is also a result of its high reactivity, which creates numerous problems in the battery environment. Lithium readily reacts with components of the electrolyte, consuming lithium to form solid-electrolyte interphases (SEIs) on its surface. The consumed lithium can no longer participate in energy storage, reducing the cell's CE. Additionally, the SEI build up can greatly increase internal resistance, reducing capacity and cycle life. As lithium is cycled, it plates and strips from the electrode unevenly, exposing fresh lithium to the electrolyte and leading to further SEI formation. Nonuniform growth can greatly thicken the electrode as pores form and can lead to growth of whisker-like lithium structures, known as dendrites. Dendrites exacerbate these issues by exposing more lithium, accelerating SEI formation. In extreme cases, dendrites can puncture the separator and cause internal short circuits that instantly render the cell inoperable. They can also break off from the bulk electrode to form dead lithium, metallic lithium that is electrically isolated and unable to participate in the electrochemical reaction. Addressing these challenges is critical before LMBs can achieve widespread commercialization.

1.3.3. Proposed Solutions

Many advancements have been made in recent years to address the challenges posed by lithium's high reactivity. The largest strides have arisen from studies on the effect of pressure on LMBs and from electrolyte development. The best performance of an LMB to date was fabricated by a team at PNNL combining these advances to produce a pouch cell with 350 Wh/kg energy density and a cycle life of 600 cycles.¹⁰

Applying pressure to LMBs has been shown to increase CE and cycle life, as well as improve lithium morphology. A study from the University of San Diego demonstrated that applying sufficient external pressure during lithium deposition onto a copper substrate reduce the porosity of the deposited lithium from 43.57% to 0.51%.¹¹ Initial cycle CE was also shown to increase with increased pressure. Other studies have supported the observation of denser lithium at higher pressures, even within the area of a coin cell depending on the type of spring used in assembly.¹² The same PNNL team that reported the best pouch cell results to date also reported that constant pressure application greatly reduces cell swelling and increases cycle life.¹³

Electrolyte development has also greatly improved CE and cycle life of LMBs in the last 10-15 years. The shift began with the push towards high concentration electrolytes, in which high concentrations of lithium salts were added to organic solvents, forming different, highly beneficial solvation structures.^{14,15} While performance was greatly improved, researchers quickly shifted to search for a cheaper alternative that could impart the same performance and similar properties while reducing the amount of expensive lithium salt required. Localized high concentration electrolytes (LHCEs) arose from this effort and have become a standard of state-of-the-art LMB electrolytes.¹⁶⁻¹⁸ LHCEs rely on mixing a high concentration of lithium salt into a solvent and then adding a diluent to increase volume while preserving the solvation structures that high concentration electrolytes form. Beyond LHCEs, a wide variety of other electrolyte formulations have been presented in recent years, including fluorinated ethers (utilized in this work), deep eutectic solvents, and high-entropy electrolytes.¹⁹⁻²³

While the optimization of pressure application and continued tuning of electrolyte formulation have greatly improved LMB performance, the rate of improvement has begun to plateau. New advancements are needed to continue to push cycle life and CE and to further

increase energy density. One area that could fuel these advances is the use of 3D current collectors for the lithium metal anode. Current collectors are traditionally foils, considered planar due to a lack of open volume within their thickness. Three-dimensional current collectors, conversely, consist of an electronically conductive structure that incorporates some variation and volume within its Z-dimension (i.e., a metal foam). While 3D current collectors are not a new idea, the body of work is far from cohesive, and many questions around their design and benefit remain unanswered.

This thesis aims to address two key gaps in the research, namely what properties of 3D current collectors consistently correlate to improved performance and the impact of 3D current collectors on performance of LMAs under conditions relevant to full cell cycling and paired with state-of-the-art electrolyte advances. The following chapter examines the scientific basis of and common themes in 3D current collector work. Two studies investigating the research questions outlined are included in chapters three and four, and a summary of all work and recommendations for further research directions are provided.

Chapter 2. Three Dimensional (3D) Current Collectors for Lithium Metal Anodes

2.1. THREE DIMENSIONAL (3D) CURRENT COLLECTOR INTRODUCTION AND DEFINITION

In the last ten years, a wide body of work has been devoted to designing and testing three dimensional current collectors for LMAs and anode-free LMBs. Copper foil has been used as the anode current collector for LIBs for years due to its high electrical conductivity and ease of processing. Researchers investigating the potential of lithium as an anode material adopted it for the same reasons. However, the challenges of low CE and cycle life that arise from plating and stripping lithium from a planar surface like foil led some to consider alternative solutions to improve cycling performance. Beyond performance, the choice of current collector also impacts energy density. Copper is dense, and while copper foil can be manufactured at thicknesses below $10\text{ }\mu\text{m}$, it still adds significant inactive mass to a cell's total mass. In attempting to reach energy densities of 500 Wh/kg and beyond, such inactive weight must be minimized as much as possible while performance remains high.

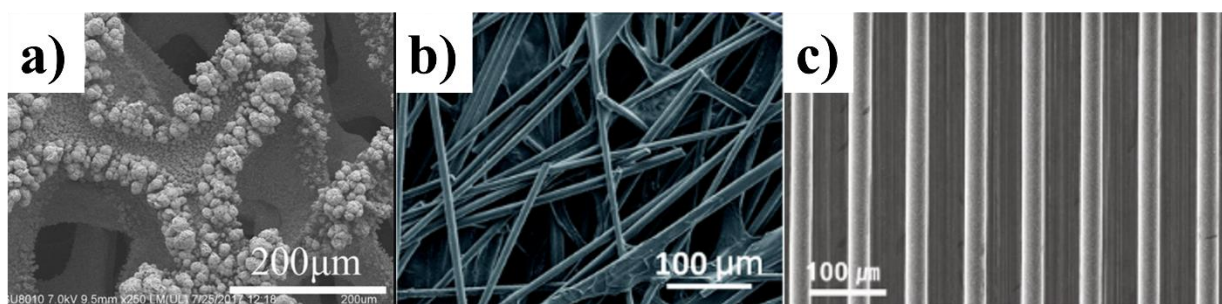


Figure 2-1: Examples of common 3D structures employed as current collector for lithium metal anodes, including (a) foam, (b) fibers, and (c) channels.^{24–26}

Three dimensional current collectors have been pursued as an alternative to copper foil in attempting to reduce mass and improve performance. The 3D descriptor arises from the 2D nature of copper foil, which has material and structure in the x-y plane, but no variation in the z direction. The concept of a 3D current collector adds structure in the z direction, providing pores and open volume into which electrolyte and lithium can penetrate. This structure can take many forms, with some common examples being foam, fiber, and channel structures (Fig. 2-1). The porosity of 3D structures reduces the density of the current collector and thus removes some inactive mass. Three-dimensional structures are also purported to stabilize the LMA over cycling, including improving lithium deposition and stripping morphology by controlling lithium deposition, containing volume expansion, and stabilizing the SEI. The remainder of this chapter describes the scientific reasoning behind the reported benefits of 3D current collectors for LMAs and provides select examples of works that use that reasoning for current collector design. Notable gaps in the 3D current collector literature will also be identified.

2.2. DENDRITE FORMATION AND SAND'S TIME

The fundamental goal of utilizing 3D current collectors for LMAs is the prevention of dendrite formation and/or propagation that leads to internal shorting. One of the most important insights into dendrite formation was reported by Henry Sand at the turn of the 20th century.²⁷ Sand mathematically described the time at which dendrite growth initiates when a metal is electroplated on a surface in a dilute solution, referred to since his publication as Sand's time.^{27,28} Sand's time defines the time required for the cations near the surface of the electrode to be consumed and their concentration to drop to zero. This absence of cations induces a strongly negative electric field which attracts additional cations and leads to rapid plating and dendrite growth. The time τ_s is defined as:

$$\tau_s = \pi D \left(\frac{C_0 e z_c}{2J} \right)^2 \left(\frac{\mu_a + \mu_c}{\mu_a} \right)^2 \quad \text{Eq. 2-1}$$

where C_0 is the initial cation concentration, e is electron charge, z_c is cation charge, J is current density, μ_c and μ_a are cationic and anionic mobility respectively, and

$$D = \frac{(\mu_a D_c + \mu_c D_a)}{(\mu_a + \mu_c)} \quad \text{Eq. 2-2}$$

in which D_c and D_a are the cationic and anionic diffusion coefficients.

From Equation 2-1, a few clear relationships can be seen. Most of the variables of interest are related to electrolyte properties and have been optimized in electrolyte formulation. One example is that τ_s is proportional to the initial concentration squared, a relationship that has pushed electrolyte develop to high concentration electrolytes as described in Section 1.3.3. However, one variable can be influenced by current collector design. The J^2 relationship to τ_s is a key contributor to the concept of 3D current collectors. While applied current density could simply be reduced to ensure dense, nondendritic growth, that luxury is not available for batteries, which must operate under a range of current density depending on the power being demanded. Therefore, methods to reduce the local current density, or the current at any particular point on the surface, while maintaining the demanded high current density on an areal basis (i.e., considering macroscopic x-y dimensions), are necessary to exploit this relationship. If a lower current can be realized, the time to dendrite growth initiation is increased and dendrites suppressed.

2.3. SURFACE AREA, CURRENT DENSITY, AND OVERPOTENTIAL

One method to decrease local current density is the incorporation of 3D structure into the electrode onto which the cation is being plated. Adding material in the z-dimension provides greater surface area per macroscopic area of the current collector. Compared to an equivalent current passed through a flat current collector, any point on the surface of a 3D current collector

would have a much lower current density. A large portion of the efforts in current collector design has been in increasing surface area, with some studies reporting specific surface areas of their current collector reaching as high as 850-950 m²/g.²⁹⁻³¹ However, it must be noted that increasing the surface area of the electrode also increases the surface area of lithium that is exposed to the electrolyte and thus SEI formation. SEI formation consumes lithium ions, reducing Coulombic efficiency. In practical high energy density batteries where electrolyte volume is tightly constrained, increased surface area may also lead to more rapid electrolyte depletion and dry out. SEI contributes to increased polarization and internal impedance with repeated cycling which further impacts cycle life. No indication of a balance of these factors has been noted in 3D current collector literature, though it would likely be greatly beneficial to current collector design.

Beyond simply reducing current density, 3D structures can be designed to direct current density to certain features and away from others. Current density increases as curvature increases in magnitude, a factor that contributes heavily to dendrite propagation as current focuses at the tip of the dendrite instead of evenly distributing across its surface. This phenomenon can be exploited in current collector design to guide lithium deposition into desired areas. Wang et. al. designed a 3D current collector with regular, circular pores and modeled that the current density in the pores was 10 times that of the planar surface, driving lithium deposition within the pore volume.³²

The reduction of current density that accompanies increased surface area has additional benefits for lithium plating and stripping. Studies have demonstrated that lower current densities correlate with improved density of plated and stripped lithium.³³⁻³⁵ At reduced current densities, the radii of lithium nuclei increase, though the density of nuclei per unit area decreases. This growth pattern leads to lower porosity within the deposited lithium volume. Denser lithium plating

and stripping reduces the amount of SEI and electrically isolated dead lithium formed, increasing CE and prolonging cycle life.

Current density additionally impacts plating and stripping overpotential as described by the Butler-Volmer equation.³⁶ Perhaps the most widely applied electrochemical equation, the Butler-Volmer equation describes local current density at an electrode surface where both a reduction and an oxidation reaction are occurring as:

$$i = i_0 * \left\{ \exp \left[\frac{\alpha_a z F \eta}{RT} \right] - \exp \left[- \frac{\alpha_c z F \eta}{RT} \right] \right\} \quad \text{Eq. 2-3}$$

where i is the current density, i_0 is the exchange current density, α_a and α_c are the anodic and cathodic charge transfer coefficients, z is the number of electrons involved in the reaction, T is temperature, R and F are the universal gas constant and Faraday constant respectively, and η is the overpotential. In a system where all other variables remain constant, a reduction in applied current density decreases the overpotential and vice versa. Overpotential relates to the energy needed to drive the redox reaction, which in LMBs is the lithium plating or stripping from each electrode. Studies have correlated reduced overpotential with improved cycle life, particularly for LMAs, and many 3D current collector works attribute success to this reduction.³⁷⁻⁴⁰

2.4. VOLUME CHANGE MITIGATION AND SEI STABILIZATION

One major drawback of utilizing LMAs in batteries is their inherent volume expansion during cycling. Because the cycling process consists of solid metal plating onto or dissolving from the LMA, a minimum 5 μm thickness change for every 1 mAh/cm^2 of lithium cycled, calculated from lithium's theoretical density, occurs each half cycle. In realistic cells, cycled lithium is not fully dense, and SEI and dead lithium build up over cycling, further exacerbating thickness increases. This volume expansion can put severe stress on battery cells and lead to failure.⁴¹ In addition to increasing the surface area of the current collector, integrating 3D structure introduces

free volume and porosity within the current collector thickness. If lithium plates within that porosity, the overall volume of the anode remains the same or very close to the initial thickness, eliminating up to tens of microns of thickness change every cycle.^{25,42–44} Within the current collector, the density of cycled lithium should also be higher due to the constraining forces of the surrounding structure. Pulverization and dead lithium formation are reduced as a result, and two major contributors to LMB death are curtailed.

Driving lithium to plate within structures can be difficult, as lithium will tend to plate on the nearest conductive surface. In batteries, that surface is typically the surface of the electrode directly facing the electrolyte and opposite electrode. To drive lithium plating within the structure, insulative materials are sometimes incorporated onto 3D current collectors to prevent lithium from plating until it reaches deeper within the structure.^{45,46} While studies have demonstrated the viability of this technique, it is typically not practical for high energy density cell design as the materials contribute additional inactive mass. Applying insulative coatings also increases process complexity significantly, greatly increasing price for limited benefit from guided lithium plating.

Suppressing thickness changes and pulverization of cycled lithium also contributes towards stabilizing the SEI, another crucial aspect of cell cycling performance.⁴⁷ When lithium cycles on a 2D surface, the large volume changes stress the SEI, repeatedly cracking it and exposing fresh lithium to the electrolyte. Because the SEI is electronically insulative, lithium preferentially plates where it cracks, leading to dendrite formation and propagation. Even if dendrite formation does not occur, additional electrolyte and lithium are consumed to form a new SEI layer where cracks form. Either the SEI on a LMA must be robust, ionically conductive, and flexible if it is to withstand the stresses of cycling and remain intact, or the stresses applied on it must be limited.⁴⁸ By utilizing 3D current collector to mitigate volume change, the stresses applied to the SEI can be

greatly reduced, preventing continuous degradation and reformation even with suboptimal SEI properties.^{49–52}

2.5. SOLID ELECTROLYTE INTERPHASE (SEI) FORMATION AND COMPOSITION

Though volume change mitigation can stabilize the SEI, a far more common way to tune SEI properties and improve cyclability is by tailoring its composition. The electrolyte components, including solvents and salts, and the initial composition of the surface of lithium all contribute to the formation of the SEI and dictate what compounds are most prevalent. Much of the electrolyte development work for LMBs revolves around this fact, striving to design electrolytes to form ideal SEIs. In the 3D current collector space, the emphasis is placed on the surface composition of the current collector to prompt the formation of beneficial compounds to improve stability. The SEI can be strengthened and Li-ion transport across the interface improved without consuming as much electrolyte.^{53,54} Elements like oxygen and fluorine are frequently claimed to improve SEI properties and have been included in 3D current collector design with good results.^{55–58} This strategy could reduce or eliminate the need for state-of-the-art electrolytes, and standard, cost-optimized electrolytes can be used while realizing improved performance.

2.6. LITHIOPHILICITY

The incorporation of additional elements beyond the based current collector material is widely seen in 3D current collector literature not only for improving SEI stability but most commonly to improve lithiophilicity. Lithiophilicity is a qualitative descriptor of lithium's affinity for a material. Thermodynamic lithiophilicity refers primarily to the wettability of molten lithium on a substrate, measured quantitatively via contact angle measurements. Lithiophilicity is also used to describe kinetic effects when measured as the initial plating overpotential in half-cell configurations. Typically appearing as a dip in voltage that occurs immediately when current is

applied, this overpotential is frequently referred to as the nucleation overpotential or nucleation barrier, as it directly relates to the energy needed to initiate nucleation of the metallic species on the surface of the electrode. For current collector studies, a material is deemed lithiophilic either if the nucleation overpotential is recorded as zero or near zero mV vs. Li (Fig. 2-2). This classification encompasses elements that alloy with lithium as well. The plating of lithium on a lithiophilic surface is often correlated with improved lithium density, elimination of dendrite growth, and reduced overpotential and consequentially nucleation barriers, all factors that contribute to improved cycle life and CE.

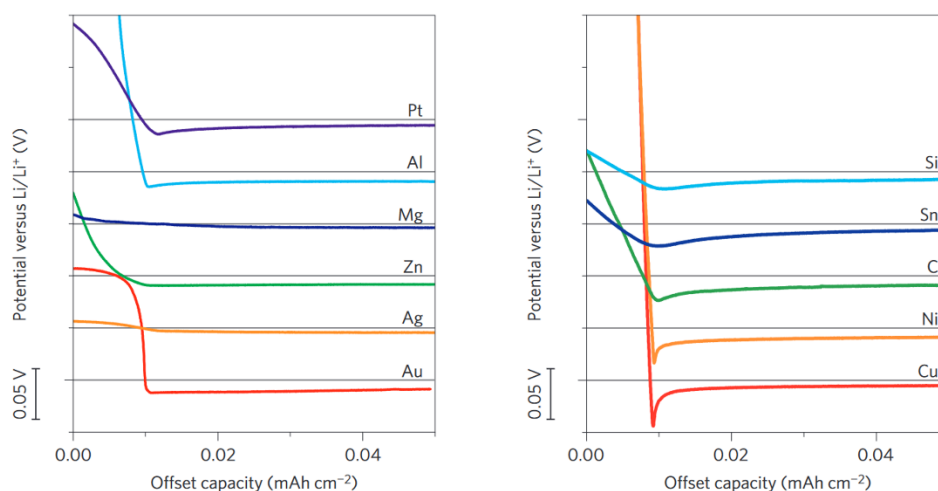


Figure 2-2: Examples of lithium plating overpotential on lithiophilic (Pt, Al, Mg, Zn, Ag, Cu, Si, Sn, and C) and lithiophobic (Ni and Cu) substrate materials.⁵⁹

There are many lithiophilic elements and materials that have been investigated over the years. Yan, et. al. verified common metallic or metalloid elements including magnesium, zinc, silver, gold, tin, and silicon in 2016.⁵⁹ Since then, these elements and compounds containing them (typically oxides) have been incorporated into 3D current collector design to further improve performance over the use of 3D structure alone.^{45,56,59–62} Similarly, organic compounds such as oxygen- and nitrogen-containing carbon compounds are reported to be lithiophilic and have been

shown to benefit performance.⁶³ With tailored incorporation into the 3D structure, lithiophilic additives are used to guide lithium deposition onto certain surfaces of the current collector, similar to the use of insulative coatings discussed in Section 2.4. This guided deposition further increases the benefit of the open volume within the structure and stabilization of the SEI aided by controlling volume expansion.^{25,56}

While improving lithiophilicity may improve lithium morphology, many of the elements used to improve lithiophilicity also alloy with lithium, most notably silicon, zinc, and tin. Though lithium deposition onto surfaces with such elements is improved, there is significant risk of parasitic reactions. In the first few cycles, extremely low CE is frequently observed as a stable alloy is formed and consumes lithium to a much greater degree than SEI formation. If the current collector can be sufficiently prelithiated (cycled against pure lithium metal until stabilized) or a lithium reservoir incorporated, the lithium loss during cycling can be mitigated. However, if the only lithium source is the cathode, alloying elements in the current collector can consume a substantial percentage of the available lithium immediately, greatly reducing the available capacity for long-term cycling.

2.7. CONCLUSIONS FROM LITERATURE AND GAPS TO ADDRESS

There are additional reports and arguments as to why 3D current collectors may improve LMA performance, but the most prevalent are presented here. From the scientific arguments employed, it is predicted that current collector design should maximize surface area and include large free internal volume. Lithiophilic and SEI-beneficial materials should also be included to achieve the best performance. Despite these insights, the body of work on 3D current collectors does not reflect a consensus on which of these factors are most important, if any must be balanced with others, or what the optimal ranges of measurable properties such as surface area and pore

volume or diameter are. Quantitative measurements of surface area are not standard and frequently unreported. When measurements are provided, studies report “high surface area” current collectors with specific surface area measurements that range from less than $0.01 \text{ m}^2/\text{g}$ to over $1000 \text{ m}^2/\text{g}$. Pore size is also inconsistently reported, if at all, complicating comparison dramatically. Chapter 3 details a study to extract trends in these properties, utilizing meta-analysis of published data coupled with statistical and data science analysis and machine learning modeling. The insights drawn from the meta-analysis will be validated with experimental investigation.

Additionally, within the 3D current collector literature, there is a glaring absence of investigation into current collector performance under LMA conditions necessary for practical LMB cell design. The vast majority of 3D current collector work focuses on results in half-cells or anode-free full cells, in which no excess lithium is provided beyond that contained within the cathode material. These cells have an N/P ratio, the ratio of anode capacity to cathode capacity, of 0. Anode-free cells are prone to early cell death, as any lithium lost to side reactions or dead lithium formation cannot be replaced. To achieve practical cycle life in LMBs, the N/P ratio must be greater than 0 to replenish lost lithium, achieved by including a lithium reservoir on the anode. Very few works examine 3D current collectors in this vital context. Chapter 4 seeks to fill that gap, particularly in investigating LMA behavior on commercially available copper current collectors that could be readily employed at scale immediately.

Though not investigated in this thesis, the lack of testing 3D current collectors in full-cells with limited electrolyte must also be noted. E/C ratio, the mass of electrolyte compared to the capacity of the battery, is a key metric in high-energy-density LMBs, as reducing electrolyte mass is a straightforward method to reduce overall cell mass. However, no 3D current collector studies

to our knowledge address this, instead using very high E/C ratios in testing. Such work is necessary if 3D current collectors are to be a viable aspect of commercial LMBs.

Chapter 3. Coupled Machine Learning and Meta-Analysis to Extract Key Properties of High-Performance 3D Current Collectors for Lithium Metal Batteries

3.1. INTRODUCTION

Despite the consensus in literature of the potential benefits of 3D current collector use as described in Chapter 2, there is a limited consensus on the relevant importance of different structural properties in 3D current collector design and how these properties should be tuned to improve performance. Numerous review articles have summarized the body of work on 3D current collectors for LMAs.^{64–69} These reviews tend to individually report performance metrics from studies, offering little or no comparison across the literature beyond tables of results. They are also frequently narrow in scope, focusing on one particular aspect of 3D current collector structures such as base material or general structure to enable deeper analysis than an overarching summary. However, it remains highly difficult to synthesize and adequately analyze published results and conclusions to guide design through traditional scientific review formats.

Meta-analysis is a method that involves collecting and reanalyzing published data to draw insights that would not be evident from considering individual studies. It is used in numerous fields, including recent studies in lithium ion battery recycling and life cycle assessments,^{70,71} but there is very limited work on its use in materials and electrode design.⁷² Meta-analyses are also frequently focused on data visualization and statistical techniques, but recent advances in and increased access to data science and machine learning (ML) have opened a new avenue for analysis. ML has been used increasingly in publications in the last year to design electrolyte formulations for LMBs but not for material or electrode design insight.^{73–78} The goal of this study is to introduce a novel analysis application and show its potential in guiding materials design.

This study aims to investigate the body of work on 3D current collectors for LMBs through meta-analysis to extract key design parameters and evaluate their impact on LMA cycling. Over 100 peer-reviewed articles containing over 220 performance records are examined with statistical approaches and ML to reveal consistent trends between 3D current collector properties, electrochemical testing parameters, and cycling performance.^{24–26,29–31,37–40,42–46,49–58,60–63,79–158} The meta-analysis reveals both testing parameters and certain structural properties have impacts on performance, though the impact of testing parameters is more consistent. Results show that a low to moderate (0.01-100 m²/g) specific surface area is beneficial to performance, as is the presence of oxygen or tin on the surface of the current collector while pore diameter does not correlate strongly to performance. Experimental validation of these conclusions supports the predicted benefits, with current collectors including oxygen and tin demonstrating higher cycle life and CE than unmodified current collectors, and a moderate specific surface area carbon-based current collector vastly outperforming a high surface area carbon-based current collector.

3.2. META-ANALYSIS

3.2.1. Dataset Compilation

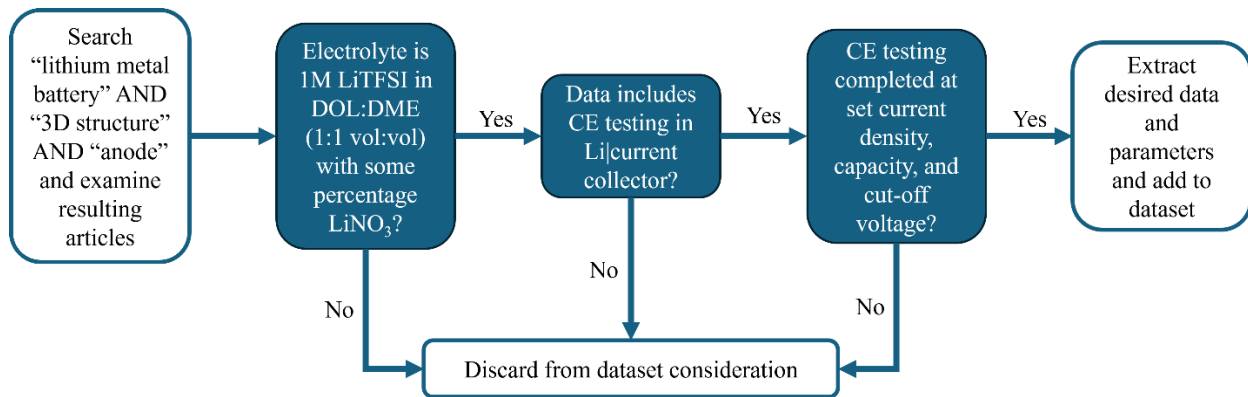


Figure 3-1: Flowchart demonstrating process of populating the dataset used in meta-analysis.

Table 3-1: Data examined in this study, including brief description, units of the feature, and the type of variable.

Data	Description	Unit	Type of Variable
Structure Properties			
Elements	Elements present in structure	N/A	Binary (1 if present, 0 if not)
Bonds	Bonds present in structure	N/A	Binary (1 if present, 0 if not)
Pore Diameter	Diameter of pores in structure	[μm]	Continuous
Surface Area	Specific surface area of structure	[m^2/g]	Continuous
Lithiophilic or Lithiophobic	Is structure lithiophilic?	N/A	Binary (1 if conductive, 0 if insulative)
Insulative or Conductive	Is structure electrically conductive or insulative?	N/A	Binary (1 if lithiophilic, 0 if lithiophobic)
Ordered or disordered	Is structure ordered or disordered?	N/A	Binary (1 if ordered, 0 if disordered)
Testing Parameters			
LiNO₃ Concentration	Concentration of LiNO ₃ in electrolyte	[wt.%]	Discreet
Current Density	Current density used for testing	[mA/cm ²]	Discreet
Capacity	Capacity used for testing	[mAh/cm ²]	Discreet
Cutoff Voltage	Voltage at which stripping is halted	[V]	Discreet
Performance Parameters			
CE	Coulombic efficiency	[%]	Continuous
Cycle Life	Cycle life of half-cell	Cycles	Continuous

The dataset for review and meta-analysis was compiled manually. Results from a Web of Science search of published peer-reviewed articles including the keywords “lithium metal battery”, “3D structure”, and “anode” were examined in order of Web of Science relevance parameter. The same keywords were input into Google Scholar to collect articles that may not have been included in the Web of Science search. Articles were assessed for relevance according to the flow chart in Figure 3-1. Dataset observations were restricted to cells cycled with an ether-based electrolyte, 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1:1 vol/vol dimethoxyethane (DME)

and 1,3-dioxolane (DOL) with some weight percentage of lithium nitrate (LiNO_3) additive. This restriction was employed due to the prevalence of this electrolyte in recent literature and the consistency of formulation, with the only variance arising in LiNO_3 concentration. Performance was recorded if articles reported CE testing in half cell configurations and at consistent testing parameters. Of over 300 articles examined, 109 fulfilled the criteria, and from them, 229 unique observations were extracted.^{24–26,29–31,37–40,42–46,49–58,60–63,79–158} Multiple studies included numerous results utilizing different substrates or testing parameters, and each variation was included as individual observations in the dataset. A brief description of the features and performance metrics extracted are provided in Table 3-1.

3.2.2. Dataset Observations

Table 3-2: Descriptive statistics of numerical parameters with missing values dropped.

Parameter [Unit]	Mean	Median	Minimum	Maximum	Number of Observations
CE [%]	97.22	98	72	99.9	219
Cycle Life	238	180	21	1400	229
Pore Diameter [μm]	76.29	27.59	0.0023	500	152
Specific Surface Area [m^2/g]	194.83	74.6	0.325	958	82
LiNO_3 Concentration [wt. %]	1.65	1	0	5	229
Current Density [mA/cm^2]	1.69	1	0.05	13	229
Capacity [mAh/cm^2]	1.44	1	0.2	10	229

Standard descriptive statistics and box and whisker plots provide initial visualization of the dataset. Statistics of each numerical parameter with missing values dropped (Table 3-2) calculate an average CE of 97.22% with a median value of 98% and an average cycle life of 238 cycles with a median of 180 cycles. The average pore diameter reported is 76.29 μm (median: 27.59 μm), and the average specific surface area is 194.83 m^2/g (median: 74.6 m^2/g). The differences between mean and median values show that the distribution of observations is skewed for these features,

Clustering also appears in the testing parameters (Fig. 3-2e-g), with the median value of current density, capacity, and LiNO_3 concentrations all equaling 1 (mA/cm^2 , mAh/cm^2 , and weight percent respectively). Of particular note, most observations recorded a cycling capacity of 1 mAh/cm^2 , which is why no box and whiskers spanning the interquartile range appears in the plot despite a wide range in reported values from 0.05 to 10 mAh/cm^2 (Fig. 3-2f). Current density (Fig. 3-2e) displays a right-skewed distribution with a similarly broad range of nearly 13 mA/cm^2 . Lithium nitrate concentration values fall within a narrower range due to solubility limits, spanning 5 weight percent (Fig. 3-2g).

Box and whisker plots are particularly helpful for identifying outliers. Outliers are defined as values outside of the interquartile range and are designated here as unfilled circles. The outliers noted here (criteria listed in Table 3-3) were excluded in some analysis that is sensitive to outliers, as will be described in later sections.

Table 3-3: Counts of dataset observations with each value of the binary properties, including electrical conductivity, structure order, and lithiophilicity (all data included, no outliers removed).

Property	Value	Number of Observations
Electrical Conductivity	Insulative	56
	Conductive	173
Structure Order	Ordered	22
	Disordered	207
Lithiophilicity	Lithiophilic	175
	Lithiophobic	54

A visualization of the distribution and counts of the elements present in the dataset observations (Fig. 3-2h) indicate frequent use of copper and carbon in current collector design, typically as the base material. Additional prominent elements include oxygen, nitrogen, and hydrogen. The counts of bonds present in the observations (Fig. 3-2i) are broader and relatively

consistent, except the most frequent bonds observed, single-bonded C to C (CC) and double bonded C to C (C=C).

3.2.3. *Extracting One-to-One and Linear Correlations*

3.2.3.1. *Pearson's Correlation Coefficient Calculations for Numerical Features*

After initial visualization and characterization, the data was analyzed to determine the key properties of high performing current collectors, beginning with examining linear correlations between each performance metric and features corresponding to structure properties. Pearson's correlation coefficients calculations, a standard data science technique, were used to quantify the correlation of numerical features to the performance metrics. In this dataset, two structure property features (specific surface area and pore diameter) and three testing parameter features (LiNO₃ concentration in electrolyte, current density, and capacity) were continuous. The Pearson's correlation coefficient method is sensitive to outliers, thus the observations with outliers as identified from the interquartile range in each variable were removed before analysis. Observations with missing values were also removed. The number of observations that remained and were included in calculations are listed in Table 3-4. Correlation coefficients were calculated using the open-source Python package Pandas, and the resulting correlation matrix was visualized as a heatmap using the open-source Python package Seaborn (Fig. 3-3a). Absolute values of coefficients from 0-0.10 designate no correlation, 0.10-0.30 weak correlation, 0.3-0.6 moderate correlation, 0.6-0.9 strong correlation, and 0.9-1 very strong correlation.

Table 3-4: Outliers removed for each variable for Pearson's correlation coefficient calculations based on interquartile range and resulting number of data points included in calculations.

Parameter [Unit]	Values	Number of Observations Remaining for Pearson's Correlation Coefficient Calculations ^[a]
CE [%]	< 95	
Cycle Life	> 580	178
Pore Diameter [μm]	> 300	119
Specific Surface Area [m^2/g]	> 600	61
LiNO_3 Concentration [wt. %]	> 3	164
Current Density [mA/cm^2]	> 5	174
Capacity [mAh/cm^2]	≥ 4 ^[b]	169

[a] Number of data points remaining after removing missing values, CE and cycle life outliers, and values outside the range dictated for each variable only.

[b] The vast majority of studies compiled in the dataset used 1 mAh/cm^2 capacity during testing. While this clustering will likely obscure correlations, the correlation coefficient was still calculated with extreme outliers removed to allow preliminary examination prior to employing machine learning modeling.

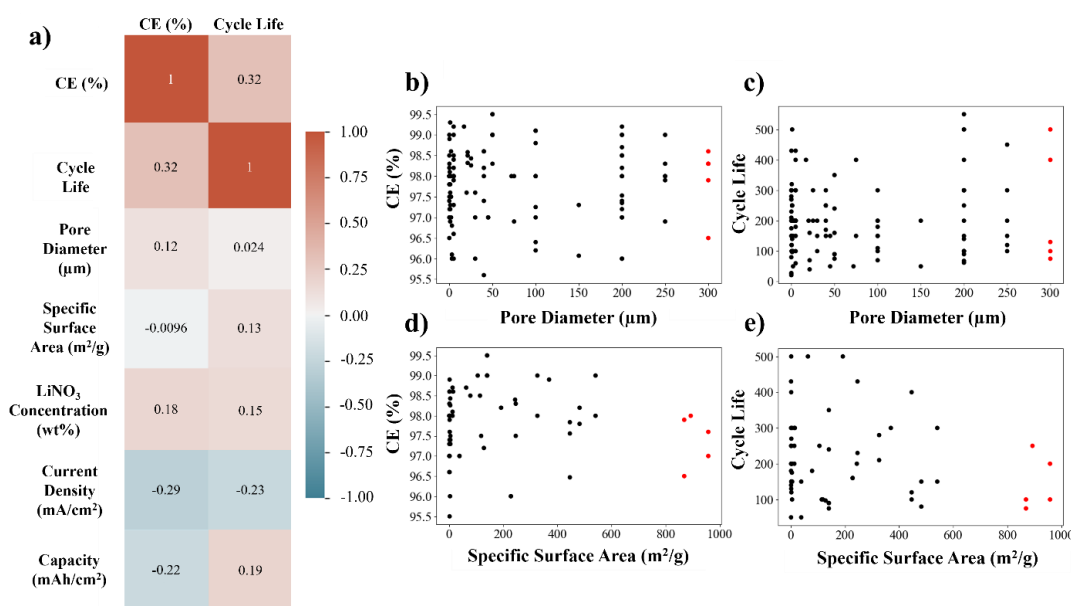


Figure 3-3: a) Pearson's correlation coefficient chart displaying the calculated coefficients between each continuous parameter and either CE or cycle life, with the dark red indicating stronger positive correlation and dark blue indicating stronger negative correlation. Scatter plots of the two numerical structural properties (b-e) support weak or no correlation when outliers are removed.

Within the structure property features, no correlation is seen between pore diameter and cycle life, nor between specific surface area and CE. A weakly positive correlation is observed between pore diameter and CE and between specific surface area and cycle life. Scatter plots of these features versus the performance parameters (Fig. 3-3b-e) visually support these conclusions. Within the testing parameters, LiNO_3 concentration is weakly positively correlated with both CE and cycle life. Capacity exhibited a weak positive correlation with cycle life and a weak negative correlation with CE, while current density showed a weakly negative correlation to both performance metrics.

The weak correlations or lack thereof between the structural properties and performance metrics are counter to much of the reported benefits of 3D structured current collectors summarized in Chapter 2, particularly concerning specific surface area. As previously described, greater specific surface area should mean a lower current density at any specific point than a low surface area electrode, assuming the current is held constant. While this benefit is weakly reflected in the correlation observed with cycle life, the same expected trend is not seen for CE. Attention must also be drawn to the exclusion of outliers, shown in the scatter plots in red (Fig. 3-3b-e). The weak positive correlation observed does not hold when the full range of observations is accounted for (Fig. 3-4). Instead, a moderate negative correlation appears between specific surface area and CE and a weak negative correlation between specific surface area and cycle life. These correlations, along with evaluation of the visualized data, show that while increasing specific surface may improve performance metrics, there is a maximum after which performance will drop. Decreased performance is likely due to the abundance of SEI build-up and associated lithium losses and impedance increases with greater lithium area exposed to the electrolyte.

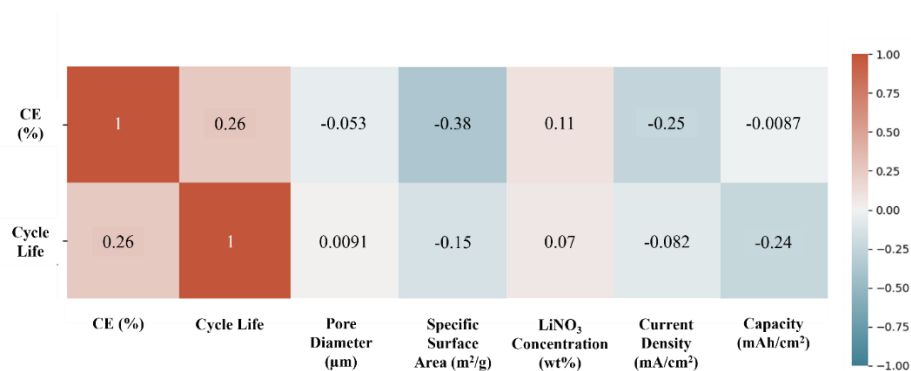


Figure 3-4: Pearson's correlation coefficient calculations with all data included (i.e., that is no outliers removed) show much different correlations for most features. In particular, a moderate negative correlation appears between CE and specific surface area that is not seen when outliers are removed.

The trends observed for the testing parameters reflect conventional understanding. Higher LiNO₃ concentration has been shown to improve lithium cyclability.¹⁵⁹ Lower current density tends to yield denser lithium that pulverizes less throughout cycling, as already discussed. Lower capacity results in higher CE for similar reasons, less losses to dead lithium. The weakly positive correlation between capacity and cycle life is unexpected; however, as seen in the visualization of the capacity distribution (Fig. 3-1f), nearly all of the capacity observations not equal to 1mAh/cm² are considered outliers. As such, the correlation calculated is not robust. If all observations are included, a weak negative correlation between capacity and cycle life is revealed (Fig. 3-4), which aligns more closely to accepted understanding.

The key insight gained from the correlation analysis is the indication that multiple features correlate, if weakly, with and thus affect the performance metrics examined here. As such, a technique that considers multiple features, such as machine learning models, is required for further analysis and optimization.

3.2.3.2. Statistical Assessment of Binary Features and Performance Metrics

The relation between performance and the binary features of the database, namely electrical conductivity, order of the structure, and lithiophilicity, were examined using appropriate statistical methods. As with the Pearson's correlation coefficient test, outliers beyond the interquartile range of CE and cycle life were removed before analysis (Table 3-5). Box and whisker plots show the median and distribution of performance metrics for each value of the binary features (Fig. 3-5a-c, e-g). The median CE values of electrically conductive and insulative observations, as well as lithiophilic and lithiophobic observations visually appear equal. Comparing ordered and disordered observations, the disordered appear to have a higher median CE than ordered. Slight differences in median cycle life are also visible with insulative observations, ordered observations, and lithiophobic observations demonstrating slightly higher median cycle life.

Table 3-5: Descriptive statistics of numerical parameters after outliers were removed.

Parameter [Unit]	Mean	Median	Minimum	Maximum	Number of Data Points
CE [%]	97.87	98.00	95.50	99.90	192
Cycle Life	193	160	21	550	212
Pore Diameter [μm]	73.49	25.18	0.0023	300	151
Specific Surface Area [m^2/g]	115.61	26.22	0.3250	541.00	74
LiNO ₃ Concentration [wt. %]	1.40	1.00	0.00	3.00	213
Current Density [mA/cm^2]	1.42	1.00	0.05	5.00	222
Capacity [mAh/cm^2]	1.15	1.00	0.20	3.00	215

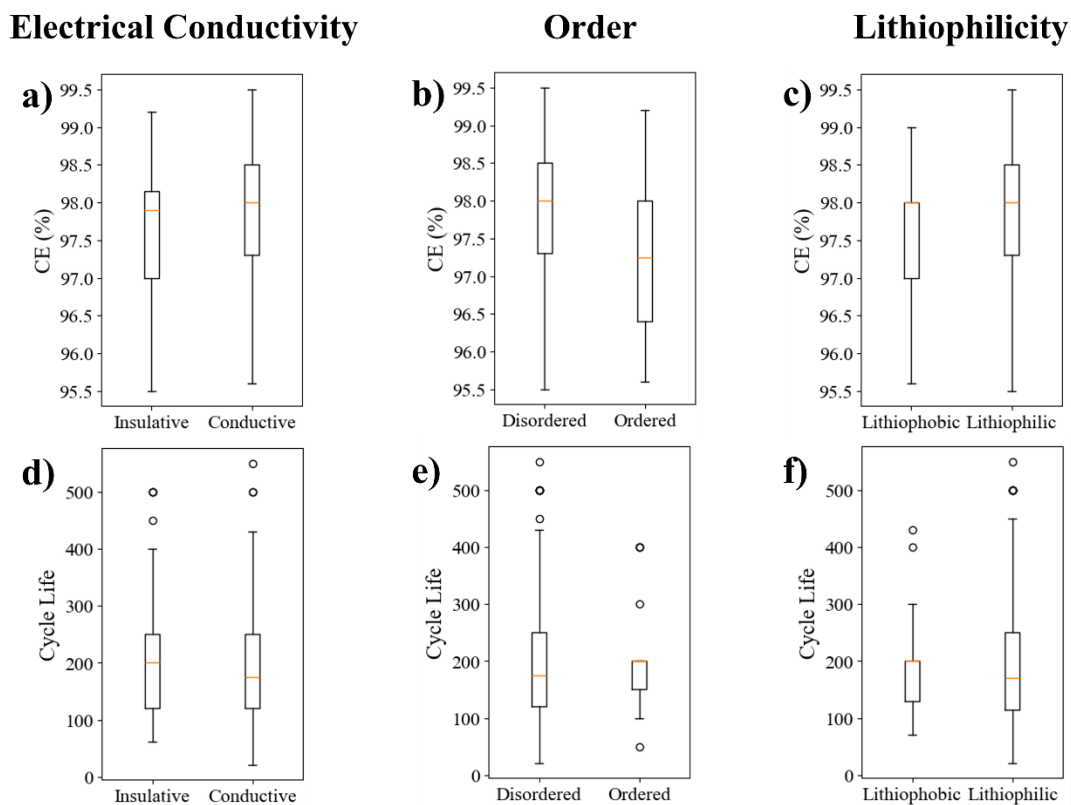


Figure 3-5: Box and whisker plots of CE (a-c) and Cycle Life (d-f) of electrical conductivity (a and d), structure order (b and e), and lithiophilicity (c and f).

To assess and quantify the differences in performance within the binary features, Mann-Whitney U tests were used to determine if the distribution of populations are stochastically different (Table 3-6).^{160,161} Mann-Whitney U analysis was chosen over Student's t-tests due to non-normal distribution of data as determined by Shapiro Wilk analysis (Table 3-7). A threshold p-value of 0.05 was set to determine significance. The null hypothesis assumes that the distributions of the populations are identical, while the alternative hypothesis states that the distribution of one of the populations is stochastically greater than the other. The analysis reveals no statistical difference in performance metric distribution for most of the binary properties except CE and order. The distribution of CE of ordered and disordered structures are statistically different, with disordered structures displaying a stochastically greater CE distribution.

Table 3-6: Results of Mann-Whitney-U statistical comparison of the distribution of performance metrics for binary properties.

	CE		Cycle Life	
Property	P-Value	Statistically Different?	P-Value	Statistically Different?
Electrical Conductivity	0.13	No	0.773	No
Order	0.026	Yes	0.364	No
Lithiophilicity	0.056	No	0.692	No

Table 3-7: P-values and interpretation of Shapiro Wilk tests of normality of CE and cycle life distribution for T-tests of binary structural features. The null hypothesis is that the data is normally distributed, and a p-value of 0.05 was set as the threshold for rejecting the null hypothesis.

CE (%)				
Binary Feature	Value	Number of Observations	P-Value	Data Normally Distributed?
Electrical Conductivity	Insulative	43	0.093	No
	Conductive	135	0.00073	No
Order	Ordered	17	0.00015	No
	Disordered	161	0.67	Yes
Lithiophilicity	Lithiophilic	139	0.0014	No
	Lithiophobic	39	0.0031	No
Cycle Life				
Binary Feature	Value	Number of Observations	P-Value	Data Normally Distributed?
Electrical Conductivity	Insulative	43	7.88×10^{-5}	No
	Conductive	135	3.14×10^{-6}	No
Order	Ordered	17	0.01	No
	Disordered	161	3.78×10^{-8}	No
Lithiophilicity	Lithiophilic	139	3.34×10^{-7}	No
	Lithiophobic	39	0.0026	No

These results also appear to contradict many claims in literature described in Chapter 2, as with the Pearson's correlation coefficient results. Insulative coatings on current collectors are claimed to encourage lithium to plate deeper within the 3D structures and thus benefit further from the internal free volume. Yet, based on this dataset, insulative structures are not seen to statistically outperform conductive structures. Similarly, lithiophilic structures are claimed to boost performance by promoting dense lithium plating and stable interfaces but do not outperform lithiophobic current collectors. The analysis indicates that the only trend is higher CE when disordered structures are employed compared to ordered structures. Consequentially, experimental validation will focus on current collectors without an ordered structure.

3.2.4. Extracting Key Structure Parameters with Machine Learning

3.2.4.1. CatBoost Decision Tree Models for Numeric Features

As linear correlation analysis revealed that multiple features impact performance, machine learning was employed to account for the collective impact of multiple factors on the performance metrics of interest in this study. The CatBoost AI-boosted decision tree ML algorithm was selected for model development due to its built-in model analysis options and its strong performance with many-variable datasets.¹⁶² Two models were developed, one to predict CE and the other to predict cycle life based on the input features of: specific surface area, pore diameter, electrical conductivity, structure order, lithiophilicity, LiNO_3 concentration, current density, and capacity. Outliers were included in the data, but only observations with values for every feature were included, a total of 55 observations. Models were optimized to root mean squared error (RMSE), and the model hyperparameters were tuned using Optuna.¹⁶³ The hyperparameters of the optimized models including both specific surface area and pore diameter are given in Table 3-8, as well as the model performance metrics. The trained models reported root mean squared error

(RMSE) values of 1.04 and 99.97 and R^2 values of 0.48 and 0.74 for the CE and cycle life models respectively. To include as much data as possible and ensure observed trends are consistent, models were also developed to predict CE and cycle life excluding specific surface area (Table 3-9 and Fig. 3-7) and excluding pore diameter (Table 3-10 and Fig. 3-8).

Table 3-8: Hyperparameters for optimized models predicting CE and cycle life based on specific surface area, pore diameter, LiNO₃ concentration, current density, capacity, lithiophilicity, conductivity, and order of 3D structures, and performance metrics. Only data points with no missing values were included in building the model, resulting in 55 observations included.

		CE Model	Cycle Life Model
	Test Size	0.2	0.25
	Random State	20	100
Hyperparameter	Learning Rate	0.037417152887452454	0.049316598301786044
	Depth of Trees	8	3
	Sample Rate for Bagging	0.8505106878711082	0.6364452126306588
	Minimum Data in Leaf	58	71
	Random Subspace Method	0.5140070595687939	0.9374673352796159
Metric	RMSE	1.04	99.97
	R^2	0.48	0.74

Table 3-9: Hyperparameters for optimized models predicting CE and cycle life based on all previously listed features except specific surface area. Only dataset observations with no missing values were included in building the model, resulting in 147 observations included.

		CE Model	Cycle Life Model
	Test Size	0.10	0.10
	Random State	40	30
Hyperparameter	Learning Rate	0.07541612079669414	0.05858755993923172
	Depth of Trees	3	2
	Sample Rate for Bagging	0.7551547401351415	0.633172021654611
	Minimum Data in Leaf	81	80
	Random Subspace Method	0.6024044836514175	0.5470285550769767
Metric	RMSE	0.95	117.27
	R2	0.57	0.25

Table 3-10: Hyperparameters for optimized models predicting CE and cycle life based on all previously listed features except pore diameter. Only dataset observations with no missing values were included in building the model, resulting in 78 observations included.

		CE Model	Cycle Life Model
	Test Size	0.15	0.20
	Random State	40	20
Hyperparameter	Learning Rate	0.0367896589724199	0.02916956365662759
	Depth of Trees	7	5
	Sample Rate for Bagging	0.918354128761683	0.9873308035386882
	Minimum Data in Leaf	38	28
	Random Subspace Method	0.9672733879170914	0.951517998262015
Metric	RMSE	0.51	100.26
	R ²	0.61	0.73

For this meta-analysis, the model performance is not the most relevant result to be analyzed, as the goal is not to input feature values to extract an accurate prediction. Rather, observing the impact of different features on the predicted output gives insight into the most important features and what feature values impact the output positively. The CatBoost algorithm includes feature importance analysis, assigning a numerical value to the influence each parameter or feature has on the model output (Fig. 3-6a and c). For both models, specific surface area and pore diameter are within the top four important features, standing as the most important features for the cycle life model. The testing parameter features have high to moderate importance for both models, indicating notable impact on predicted performance. LiNO₃ concentration was deemed the most important features in predicting CE but less important for predicting cycle life. Generally, the binary structural property features show low importance, apart from electrical conductivity contributing highly to the CE model.

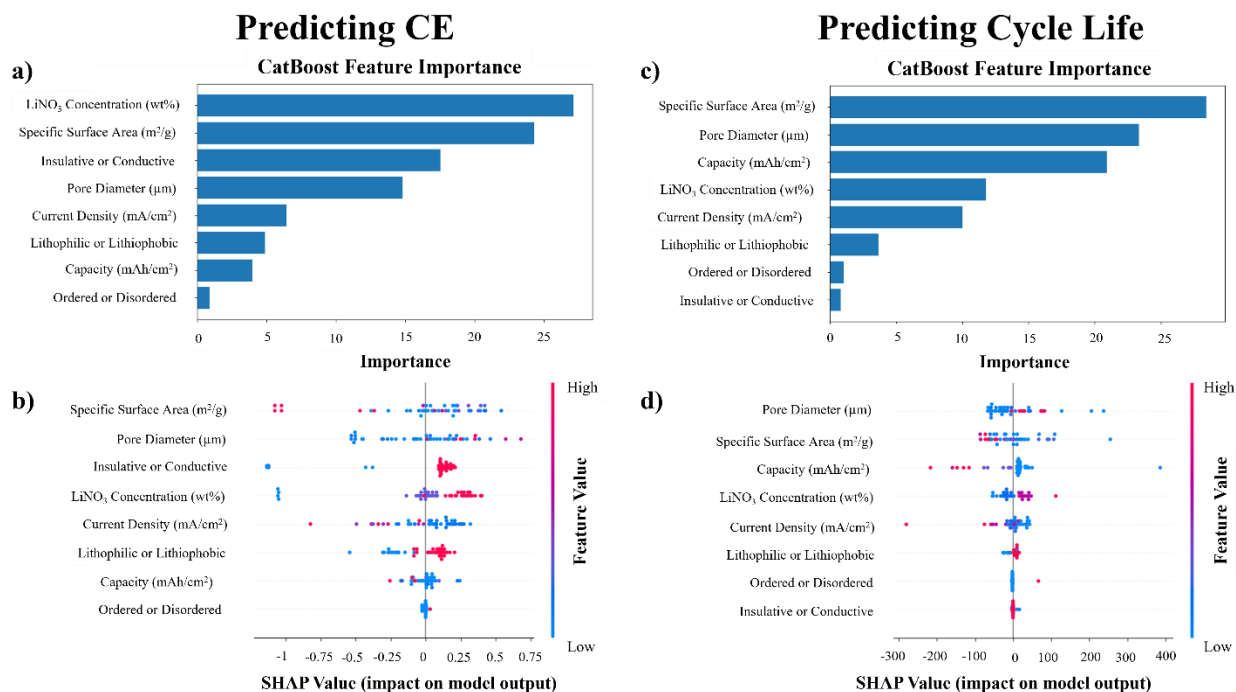


Figure 3-6: Analysis of CatBoost machine learning models predicting CE (a-b) and cycle life (c-d) provides quantification of the impact of input features on model output as feature importance (a and c), and SHAP analysis shows clear trends in input feature values on model output (b and d).

Additional analysis beyond feature importance reveals how the values of features affected the model and in what direction. Shapley Additive Explanations (SHAP) are a common method to analyze ML models.^{164,165} When examining structural property features, there are few clear trends seen. The clearest trends are visible for the binary features. For the CE model (Fig. 3-6b), there is distinct clustering of high electronic conductivity and high lithiophilicity values in the direction of positive model output impact. The high values correspond to conductive and lithiophilic values respectively, and the clustering indicates that conductive and lithiophilic structures may show higher CE. A similar clear trend is seen to a weaker extent for lithiophilicity in predicting cycle life (Fig. 3-6d) but not for electrical conductivity. For pore diameter and surface area, it is difficult to parse any trends from the data. For both CE and cycle life, there appears to

be a cluster of moderately low surface area values that have a positive impact on the model output. For pore diameter, values at the lower extreme of the range generally push the model output lower, though some low to moderate values contribute to increased model output. Most high pore diameter values impact both models positively. Similar trends are observed in the other models created (Figs. 3-7 and 3-8).

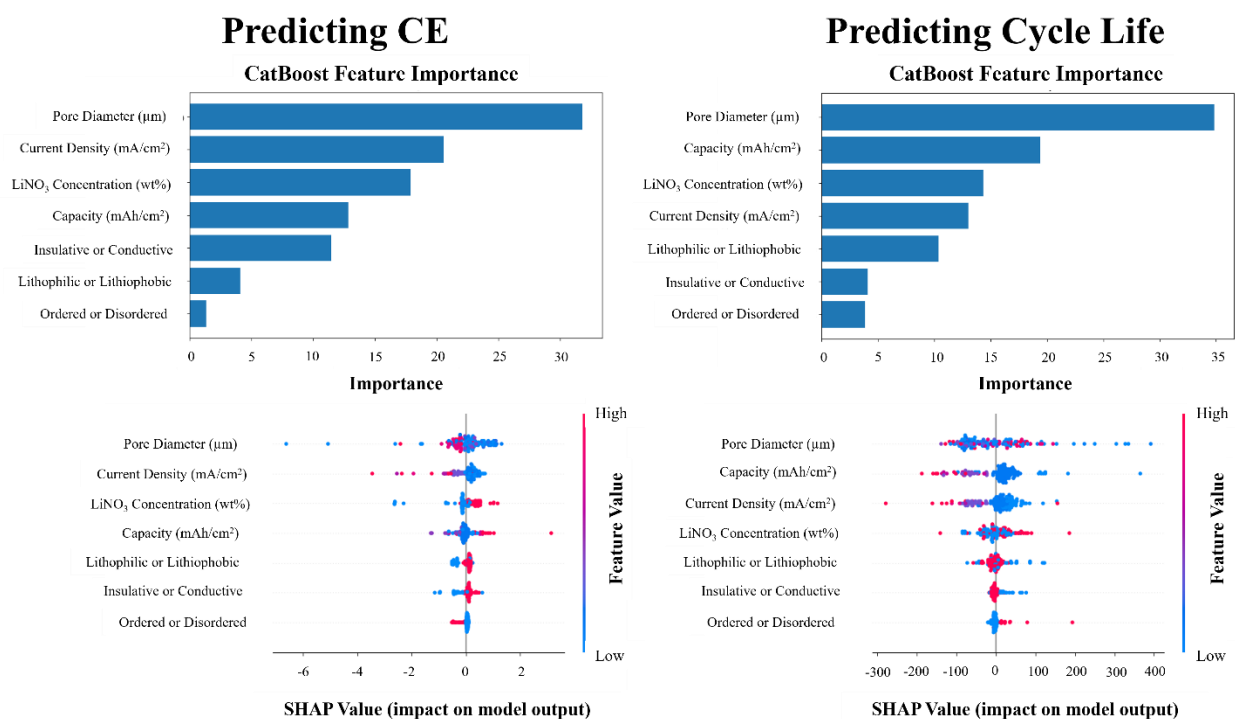


Figure 3-7: Analysis of CatBoost model predicting CE and cycle life with input features of pore diameter, electrical conductivity, structure order, lithiophilicity, LiNO_3 concentration, current density, and capacity shows similar trends to the model that also included specific surface area as an input.

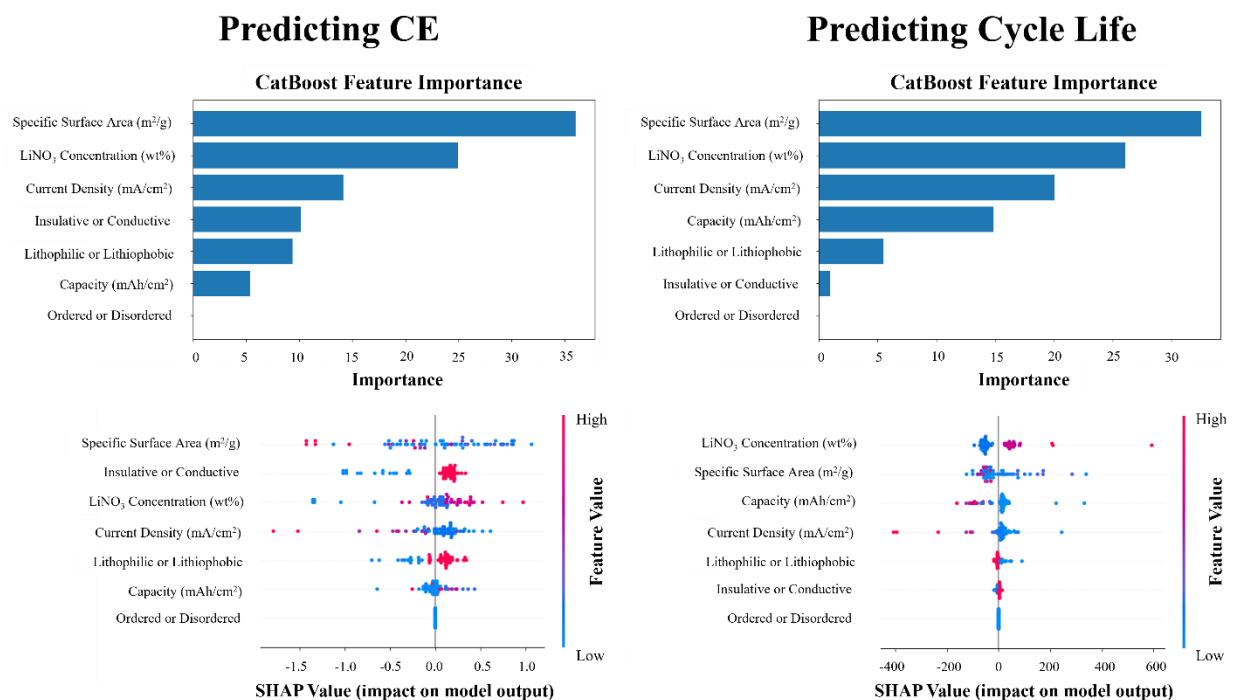


Figure 3-8: Analysis of CatBoost model predicting CE and cycle life with input features of specific surface area, electrical conductivity, structure order, lithiophilicity, LiNO₃ concentration, current density, and capacity shows similar trends to the model that also included pore diameter as an input.

Beyond the structural property features, trends are also visible in the testing parameter features. LiNO₃ concentration strongly impacts the predicted CE, with higher values having a clear positive impact and low values showing a strong negative impact. The impact on predicted output for the cycle life model is weaker, but the same clustering of high values positively impacting output is visible. Low current density values are clustered on the positive model output side. The LiNO₃ concentration and current density impacts align with conventional understanding and the correlation calculations in section 3.2.3.1. Lower capacity values show positive impact on CE and cycle life predictions, also agreeing with conventional understanding. These findings show that testing parameters have significant impact on performance metrics in half cell testing. The

impact is much more consistent and trends much more evident than for any structural parameter evaluated here. These results emphasize the need for accurate reporting of cycling procedures and testing parameters in published studies, particularly as meta-analyses and machine learning based on published data become more prevalent.

Based on these results, a structure with moderately low surface area, on the order of 0.01-10 m²/g, and pore diameters on the order of microns or larger would be predicted to give higher CE and longer cycle life than a structure with very high specific surface area or very small pores. These conclusions will be reflected in the current collectors chosen for experimental validation.

3.2.4.2. *Self-Organizing Maps (SOMs) for Element and Bond*

A different machine learning approach was employed to determine trends between the presence of certain elements and bonds and performance metrics. Self-organizing maps (SOMs) are a form of unsupervised machine learning that reduces the dimensionality of data and clusters observations accordingly. SOMs were produced using the open source Python Library for Self-Organizing Maps (SOMPY).¹⁶⁶ Maps were organized based on the performance metric features (CE and cycle life), structural property features (pore diameter and specific surface area), and testing parameters (LiNO₃ concentration, current density and capacity) into a 10x10 map to encompass all data and enable clear visualization. Training was completed through competitive learning to minimize both topographical and quantization error and accomplished locally on a 1.7 GHz Intel Core™ i7-135SU in 1.91 seconds. The corresponding values of each feature of the observations in each map location are displayed in heat maps for easy visualization of trends (Fig. 3-9). As with the CatBoost modeling, to incorporate as much data as possible, maps were also calculated excluding specific surface area (Fig. 3-10a), excluding pore diameter (Fig. 3-10b), and excluding both (Fig. 3-11) and compared for consistency. Areas of interest, where CE and cycle

life are both high, are designated by black boxes and superimposed on all heat maps. The map including all features had a topographical error of 0.009 and quantization error of 0.6766.

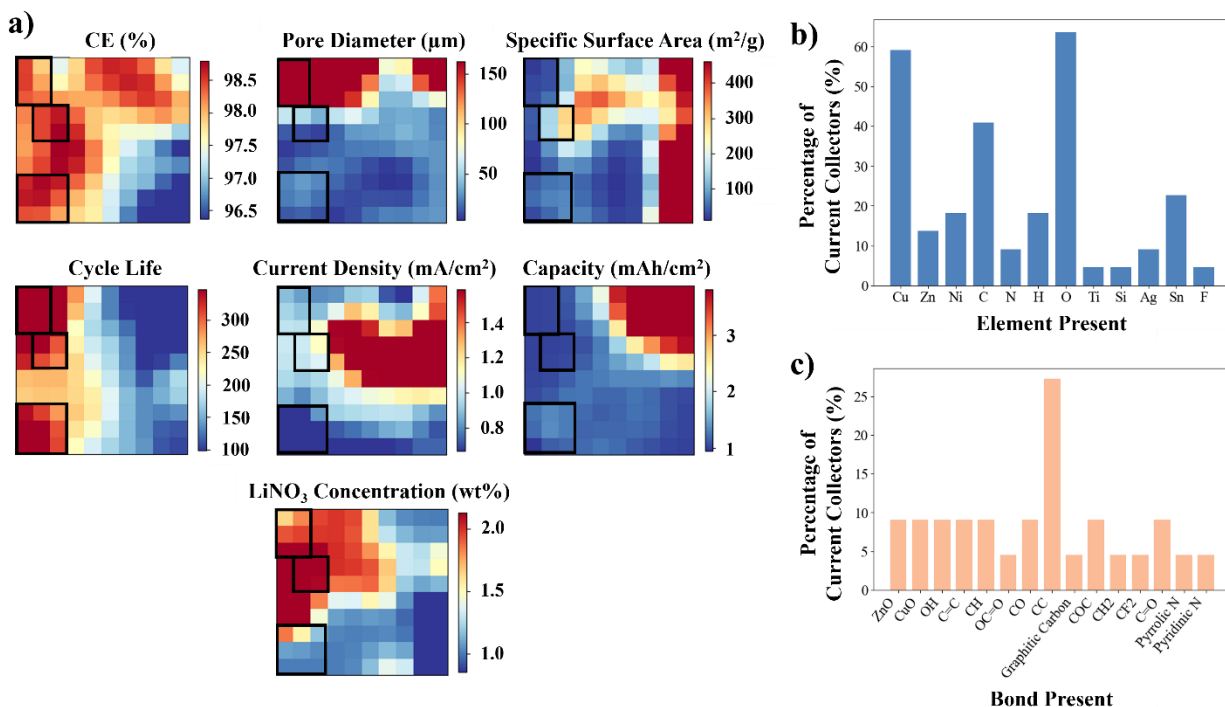


Figure 3-9: a) Heat maps of the performance metrics and continuous properties of current collectors based on a self-organizing map (SOM) with areas of interest, demonstrating high CE and cycle life, denoted by black boxes and superimposed on all heat maps for comparison. Based on SOM grouping, the percentage of structures with each element (b) and bond (c) present that fell within the areas of interest are presented.

The trends in the SOM model largely align with those observed from the CatBoost models. Low to moderate specific surface is observed in the regions corresponding to high CE and cycle life. A range of pore diameters also correspond to these regions, consisting of small to moderate diameters as well as some very large diameters. As observed in the CatBoost models and aligning with conventional understanding, low current density and capacity align with high CE and long cycle life. So too do moderate to high LiNO_3 concentrations, though a broader range is observed

than reflected in the CatBoost models. Most importantly, observations with no LiNO_3 additive overwhelming corresponded with low CE and cycle life. These trends are also observed in the SOMs excluding specific surface area (Fig. 3-10a), excluding pore diameter (Fig. 3-10b), and excluding both (Fig. 3-11), indicating that they hold across wider ranges of observations.

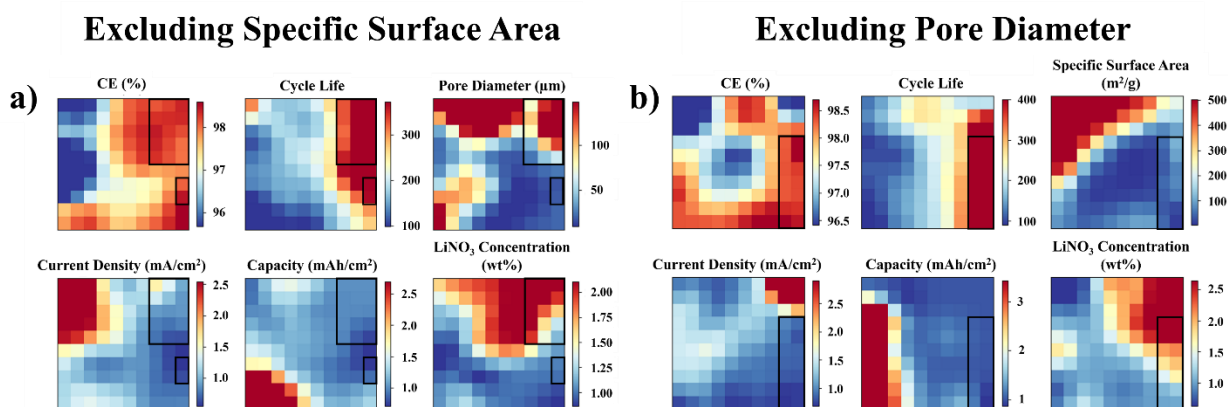


Figure 3-10: Heat maps of the performance metrics and continuous properties of current collectors based on self-organizing map (SOM) with input features of a) CE, cycle life, pore diameter, LiNO_3 concentration, current density, and capacity and heats maps b) CE, cycle life, specific surface area, LiNO_3 concentration, current density, and capacity show similar clustering to the model with both pore diameter and specific surface area included. Areas of interest, demonstrating high CE and cycle life, are denoted by black boxes and superimposed on all heat maps for comparison. The model excluding specific surface area had a topographical error of 0.009 and quantization error 0.8273, and the model excluding pore diameter had a topographical error of 0.007 and quantization error 0.6566.

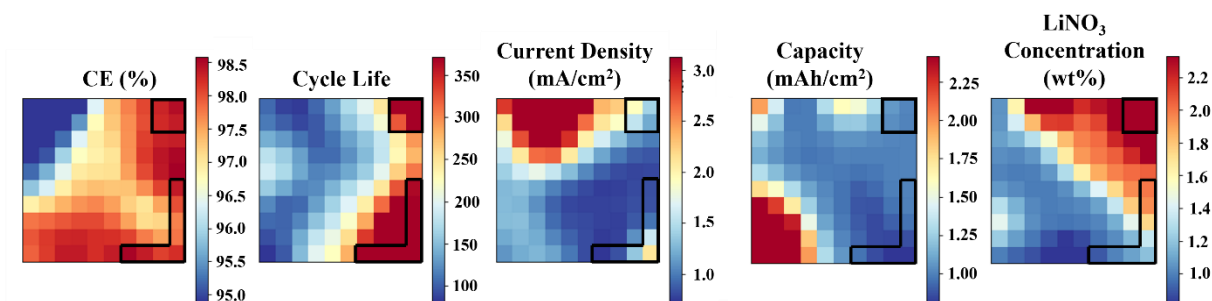


Figure 3-11: Heat maps of the performance metrics and continuous properties of current collectors based on self-organizing map (SOM) with input features of CE, cycle life, LiNO₃ concentration, current density, and capacity reveal similar clustering as seen when pore diameter and specific surface area were also included as an input feature. The model had a topographical error of 0.011 and quantization error 0.5992.

Based on the clustering in the SOM, the observations in the regions of interest were extracted and the elements and bonds present analyzed. Fig. 3-9b and c show the percentages of observations in the regions of interest with each element and bond. The most common elements likely to be used as a base material were copper and carbon, and the most common additional element was oxygen. Oxygen may be beneficial as its presence within or on the surface of a current collector could lead to the formation of Li₂O. Multiple studies in the last 2-5 years have proven that the presence of Li₂O in the SEI is beneficial for LMB performance.^{167–169} Most work has focused on tailoring electrolytes to increase the percentage of Li₂O in the SEI, and the contribution of surface oxygen species to its presence has not been rigorously studied. While this contribution will not be systematically investigated here, the presence of oxygen and its impact on performance will be evaluated in experimental validation. CuO is also electronically insulative and may contribute to the formation of other insulative species at the surface of lithium plating, preventing excess SEI formation.

Tin (Sn) is also present in a relatively high percentage of observations grouped in the area of interest, particularly in comparison to other metallic elements touted for their lithiophilicity, including Si, Ag, and Au, and to its frequency in the observations used for training (Fig. 3-12). Tin is frequently used in anodes for LIBs, either as an alloy with lithium or incorporated with other compounds such as TiO_2 ,^{170–173} and Li-Sn alloys have been shown to be a beneficial substrate for lithium plating.¹⁷⁴ As such, the presence of Sn may lead to denser lithium deposition and stripping, improving cycle life and stabilizing CE. The studies included in this meta-analysis most frequently utilize nano- or microparticles of Sn incorporated into a current collector framework,^{60,110,118,134,155} and a similar approach will be used in experimental validation to show tin's impact on performance metrics.

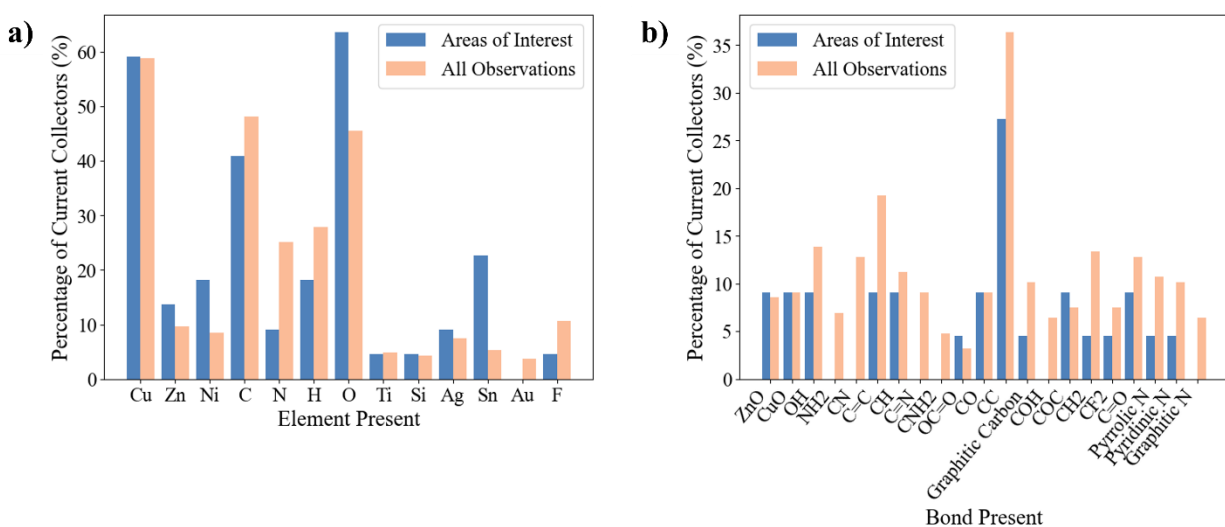


Figure 3-12: Percentage of observations that fell within the areas of interest in the SOM analysis with each element (a) and bond (b) present in the structure compared to the percent in all observations used in training the SOM reveal if any element or bond disproportionately appears in observations with high CE and cycle life compared to its overall prevalence in the dataset.

3.2.5. *Conclusions of Meta-Analysis*

Based on the combined observations of the dataset, linear correlation analysis, and machine learning investigation, several conclusions are evident. Regarding structure properties of current collectors for LMAs, a low to moderate ($0.01\text{-}100\text{ m}^2/\text{g}$) specific surface area correlates to high performance metrics than high specific surface area. No strong correlation between pore size and performance was observed, thus a variety of pore sizes can be used. Disordered structures were evaluated to have a higher CE distribution than ordered structures. No differences were observed in performance metrics between lithiophilic and lithiophobic current collectors, nor between electronically insulating and conducting materials. The presence of oxygen and of tin on a copper or carbon substrate correlates with high performance. No bonds were shown to correlate significantly with performance.

3.3. EXPERIMENTAL VALIDATION

3.3.1. *Methods*

3.3.1.1. *Current Collector Description, Fabrication, and Preparation*

Following meta-analysis, experimental testing was performed to validate the conclusions drawn. Six current collectors were selected and prepared. Copper foil was selected as the baseline two dimensional (2D) current collector. Two carbon-based current collectors served to compare performance based on specific surface area (Fig. S8), and three copper foam current collectors allowed for comparison based on the presence of various elements. One was left unaltered (CF), one was oxidized to introduce oxygen species (OCF), and one was plated with tin microparticles (SnCF) (Fig. 3-13).

The control current collectors, copper foil (12 μm thick) and unaltered copper foam (100 μm thick, MTI, Corp.) were washed with 1M hydrochloric acid for 15 seconds to remove surface oxidation and contamination, then triple rinsed in water and ethanol.

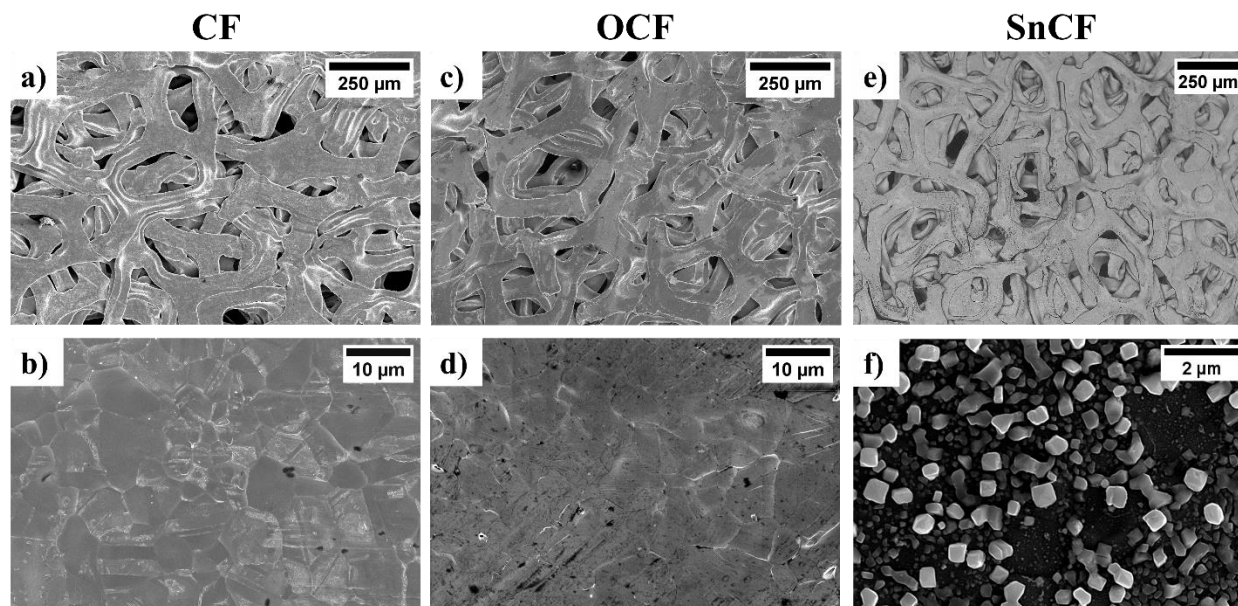


Figure 3-13: SEM images at low magnification (a, c, e) and high magnification (b, d, f) of the copper foam-based current collectors used in experimental validation, including a-b) unaltered copper foam (CF) with a few dark oxidation spots; c-d) oxidized copper foam (OCF) with a much higher density of dark oxidation areas; and e-f) copper foam with tin microparticles (SnCF) with 0.5-1 μm diameter cubic Sn microparticles.

For the carbon sample, an activated carbon current collector was purchased from NEI Corporation to represent extremely high specific surface area (Fig. 3-14a). The current collectors had a loading of 0.5 mAh/cm^2 with 90:5:5 weight ratios of activated carbon:PVDF binder:super P. The thickness averaged 30 μm .

Carbon fiber paper was purchased from Toray to represent a sample with moderate specific surface area. The paper was purchased with a 10wt% PVDF surface coating. To remove the

coating, the paper was heated to 600°C at 10°C/min under an argon atmosphere, held at 600°C for 5 hours, then allowed to cool to room temperature. This process pyrolyzed the PVDF and removed any fluorine without affecting the structure of the carbon fibers themselves (Fig. 3-14b).

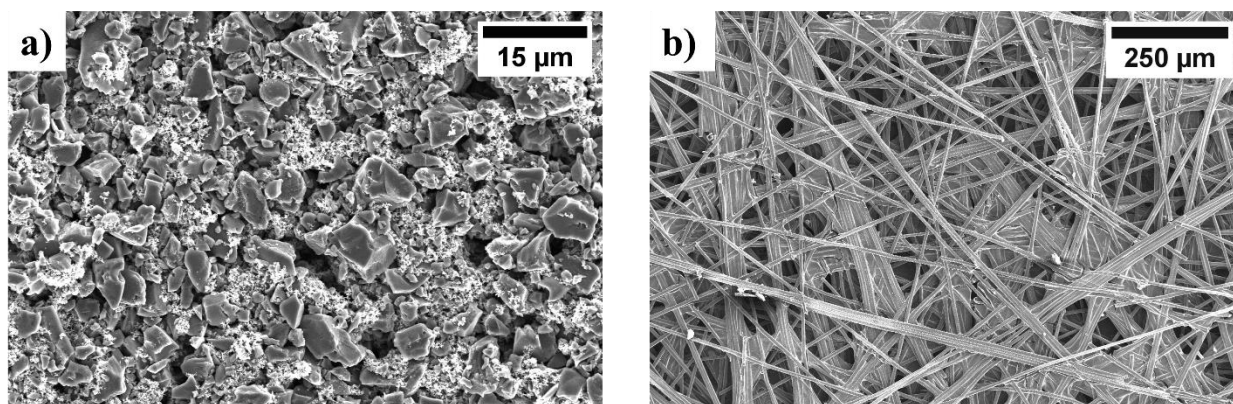


Figure 3-14: SEM images of the carbon-based current collectors chosen for experimental validation show a) the activated carbon particles; and b) carbon fibers.

To prepare the copper foam with oxygen, the unaltered foam was heated to 100°C at 2.5°C/minute under ambient atmosphere, held for 24 hours, then allowed to cool to room temperature.¹⁷⁵ The copper foam with tin microparticles was prepared via electrochemical plating in the form of contact plating. Aluminum foil (MTI, Corp) and the unaltered copper foam were immersed in 0.05M Sn(II)Cl₂ solution and the copper held in contact with the aluminum for 30 seconds. Aluminum has a much higher oxidation potential than copper (1.676V compared to -0.3419V vs. SHE).¹⁷⁶ Thus, when the two metals are in contact in the presence of Sn²⁺, the solid aluminum will oxidize to Al³⁺ and dissolve in solution while the tin will reduce to Sn(s). This plating method resulted in cubic Sn particles with side lengths of 0.5-1 μm (Fig. S10f). The current collector is similar in concept to work published by Luan, et. al.,⁶⁰ but the method was arrived upon independently. All samples, carbon- and copper-based, were dried overnight in a vacuum oven before transfer into a glovebox for cell assembly.

3.3.1.2. *Physical and Chemical Characterization*

3.3.1.2.1. *Pore Size Determination and Surface Area Measurement*

Pore size was measured from secondary electron microscope images of each current collector. Imaging was performed using a Thermo Fisher Scientific Apreo 1 at 5kV and 0.1 nA beam current. The images were analyzed using the ImageJ software. The diameters of the pores were manually determined then measured by the software. At least 25 pores were measured for each current collector.

Surface area was measured using Brunauer-Emmett-Teller (BET) characterization. Nitrogen was used as the absorbate with bath temperature of 77.35K. Degassing was performed under vacuum at 100°C for 12 hours.

3.3.1.2.2. *Elemental Composition and Bonding Environment Determination*

Elemental composition and bonding environment were determined for the unaltered copper foam, oxidized copper foam, activated carbon, and carbon fiber paper using X-ray photoelectron spectroscopy (XPS). All XPS spectra were taken on a Kratos Axis-Ultra DLD spectrometer. This instrument has a monochromatized Al K α X-ray and a low energy electron flood gun for charge neutralization. X-ray spot size for these acquisitions was on the order of 700 x 300 μ m. Pressure in the analytical chamber during spectral acquisition was less than 5 x 10⁻⁹ Torr. Pass energy for survey and detailed spectra (composition) was 80 eV, and pass energy for the high-resolution spectra was 20 eV. The take-off angle (the angle between the sample normal and the input axis of the energy analyzer) was 0°, equating to a sampling depth of approximately 100 Å. The Kratos Vision2 software program was used to determine peak areas and to calculate the elemental compositions from peak areas. CasaXPS was used to peak fit the high-resolution spectra. For the

high-resolution spectra, a Shirley background was used, and all binding energies were referenced to the C 1s C-C bonds at 284.5 eV.

Elemental composition was evaluated for the copper foam with tin microparticles via energy dispersive X-ray spectroscopy (EDS). The measurements were taken using a Thermo Fisher Scientific Apreo 1 at 15kV acceleration voltage with a dwell time of 10 μ s.

3.3.1.3. *Electrochemical Testing*

Cycling experiments were completed using 2032 coin cells assembled in an argon glovebox (Vacuum Technologies, Inc.) in which the oxygen and water content were maintained below 0.01 ppm. A mixture of 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (Thermo Fischer) in 1:1 vol/vol dimethoxyethane (DME) (Gotion) and 1,3-dioxolane (DOL) (Sigma Aldrich) with 2 wt.% LiNO₃ additive (Sigma Aldrich) was chosen as electrolyte. Coin cells were assembled with a 100 μ m thick lithium chip counter to the current collector, two 16 μ m thick polyethylene separators (Nanoshel LLC), and 80 μ L of electrolyte. Two spacers (one 1 mm and one 500 μ m) and a wavy spring (1.2 mm) (MTI, Corp.) were also included to provide adequate internal pressure for cycling. Cells were crimped with a pressure of 800 mPa. Cells were cycled on an Arbin Instruments cycler through three formation cycles at 50 μ A/cm² in a voltage range of 0.01-1V followed by repeated plating to 1 mAh/cm² at 1 mA/cm² and stripping at the same current density to 1V.

3.3.2. *Results and Discussion*

3.3.2.1. *Current Collector Characterization*

As noted in Section 3.3.1.1, two carbon-based current collectors served to compare performance based on specific surface area. The activated carbon (AC) current collector had a specific surface area of 1500 m²/g, and the carbon fiber paper (CFP) current collector had a specific

surface area of $0.976 \text{ m}^2/\text{g}$, within the range of values correlated to high performance. The carbon current collectors had average pore diameters of $1.43 \text{ }\mu\text{m}$ and $38.9 \text{ }\mu\text{m}$ respectively. X-ray photoelectron spectroscopy (XPS) confirmed that the activated carbon current collector consists mainly of graphitic carbon with an asymmetric peak appeared at 284.5 eV , with low concentrations of C-C and C-H bonds visible at 284.8 eV , C-OH and C-O-C at 286.2 eV , satellite pi-pi* bonds at 288.7 eV , and CF-based compounds at 290.6 eV (Fig. 3-15a). The compounds containing oxygen and fluorine likely originate from the PVDF binder used to fabricate the electrode. The carbon fiber paper consisted entirely of graphitic carbon with an asymmetric C=C peak appearing at 284.5 eV (Fig. 3-15b).

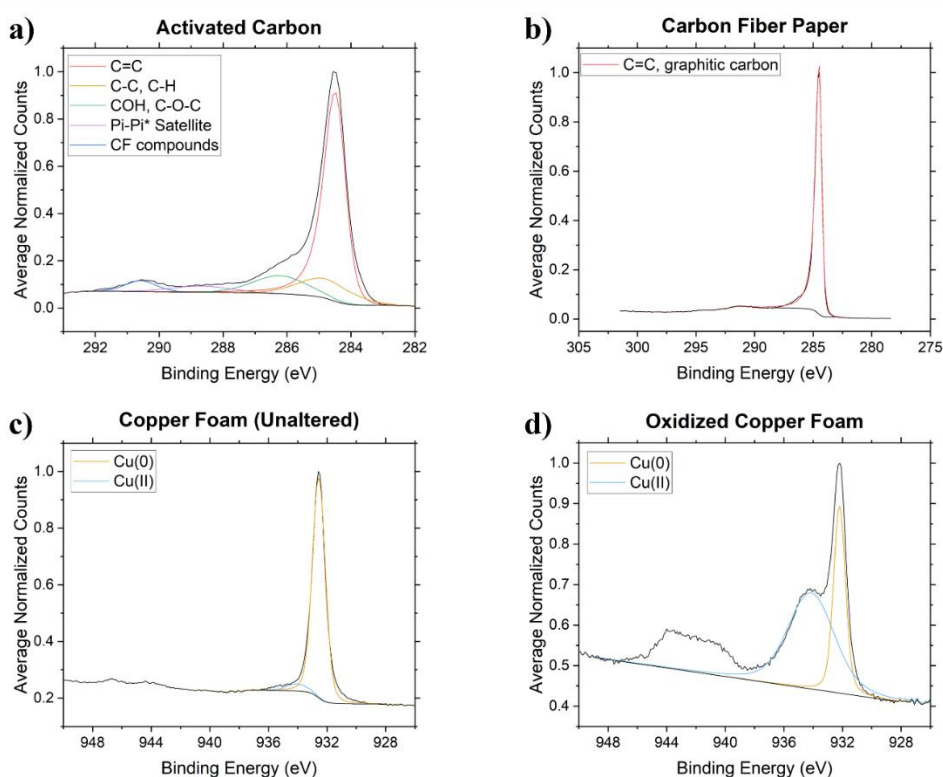


Figure 3-15: X-ray photoelectron spectra of the a) activated carbon, b) carbon fiber paper, c) unaltered copper foam, and d) oxidized copper foam current collectors were acquired to determine elemental composition and bonding environments.

Three copper foam current collectors (CF, OCF, and SnCF) allowed for comparison based on the presence of various elements. All copper foam-based current collectors had an average pore diameter of 120 μm , and their specific surface areas were similar with CF and OCF measuring 0.054 m^2/g and SnCF measuring 0.082 m^2/g . XPS confirmed the presence of a native oxide layer on the OCF current collector, with a Cu(0) peak at 932.2 eV and a Cu(II) peak appearing at 934.2 eV (Fig. 3-15d). The Cu(II) species are most likely Cu(II)O based on the fabrication method and the shape of the satellite peaks. The Cu(II) peak is much more prominent in the OCF spectrum than the CF spectrum, confirming significant difference in surface chemistry (Fig. 3-15c). The composition of the plated tin on the SnCF was confirmed via energy dispersive X-ray spectroscopy (EDS), which showed cubic tin particles with dimensions of 0.5-1 μm on the copper foam surface with no noticeable alloying (Fig. 3-16). The average loading of tin on the SnCF current collectors was $0.7 \pm 0.1 \text{ mg}/\text{cm}^2$. Table 3-11 summarizes the features of each current collector as would be recorded in the dataset.

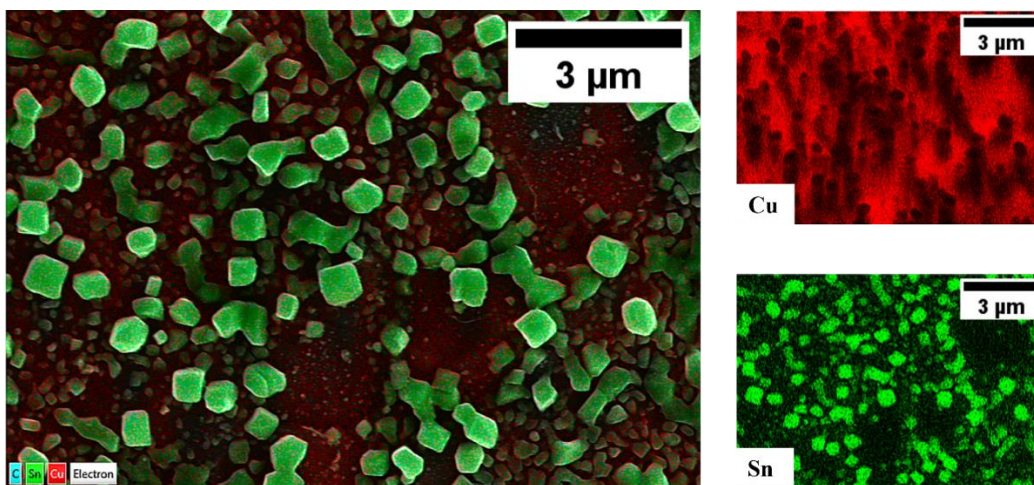


Figure 3-16: EDS analysis of the SnCF shows that the microparticles consist of pure tin with no observable alloying occurring and no significant contamination.

Table 3-11: Features of current collectors employed for validation as would be included in the dataset.

	AC	CFP	CF	OCF	SnCF
Elements Present	C, O, F, H	C	Cu, O	Cu, O, H	Cu, Sn
Bonds Present	C-C, C=C, COH, C-O-C, CF compounds	C=C	CuO	CuO, Cu(OH) ₂	N/A
Pore Diameter [μm]	1.43	38.9	120	120	120
Surface Area [m²/g]	1500	0.976	0.054	0.054	0.082
Lithiophilic or Lithiophobic	Lithiophilic	Lithiophilic	Lithiophobic	Lithiophilic	Lithiophilic
Insulative or Conductive	Conductive	Conductive	Conductive	Insulative	Conductive
Ordered or Disordered	Disordered	Disordered	Disordered	Disordered	Disordered

3.3.2.2. *Cycling Performance*

To evaluate performance, coin cells were assembled with each current collector placed opposite lithium metal. Cell assembly and detailed cycling information are provided in Section 3.3.1.3. To briefly reiterate, 1M lithium bis(trifluoromethanesulfonyl)imide LiTFSI in 1:1 1,3-dioxlane (DOL): dimethoxyethane (DME) with 2wt% LiNO₃ was chosen as the electrolyte. For cycling, capacity was set to 1mAh/cm² at a current density of 1mA/cm², and the cutoff voltage was set to 1V. End of cycle life was set to when the CE dropped below 90% for all cells except those with AC current collectors. For AC cells, CE decreasing below 60% or exceeding 102% marked the end of cycling.

Cycling performance as CE plotted against cycle number for select cells reveals distinct differences between current collectors (Fig. 3-17). CFP widely outperformed any other current collector, reaching 340 cycles and maintaining an average CE of 99.94% throughout cycling (Fig.

3-17a). In contrast, AC never reached a stable CE over cycling and was prone to internal soft shorts, in which the CE recorded over 100% (Fig. 3-17a). It reached 70 cycles before the CE dropped below 60% with an average CE of 89.2%. CFP also demonstrated higher CE in initial cycles compared to AC (inset of Fig. 3-17a). As was predicted in the meta-analysis, the CFP with moderate specific surface area and moderate pore size recorded better performance than the AC with extremely high specific surface area and small pore size.

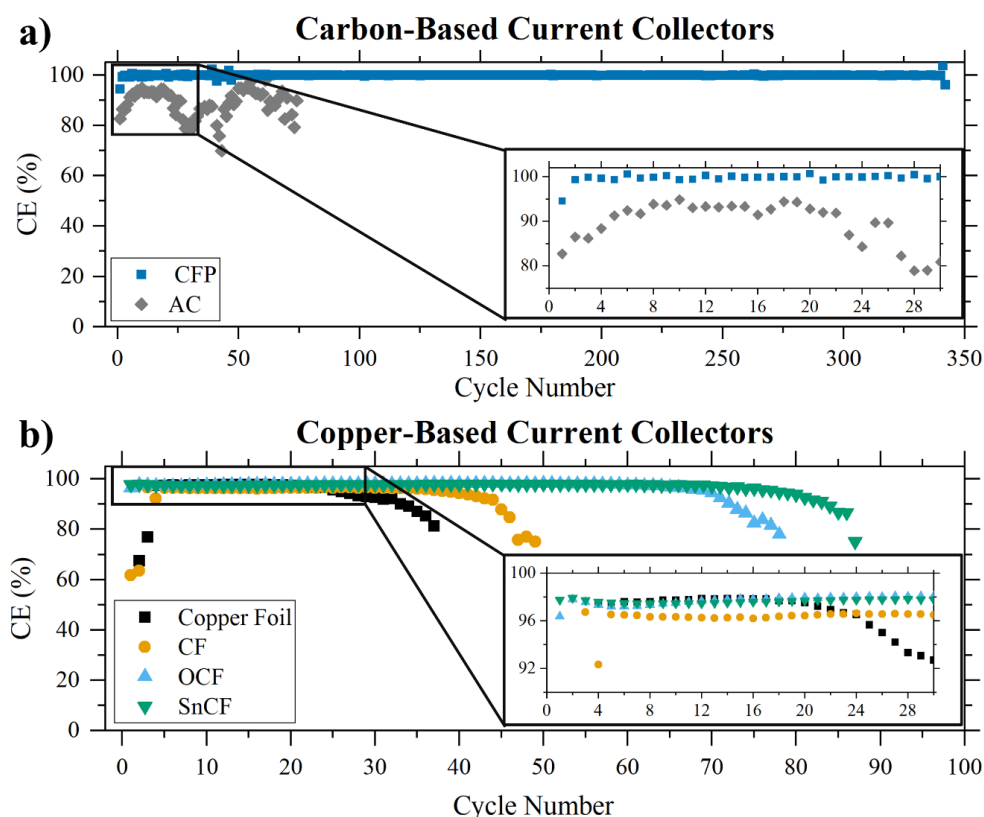


Figure 3-17: Cycling performance of half-cells with (a) carbon-based and (b) copper-based current collectors with initial 30 cycles magnified to evaluate initial CE validate the trends identified in the meta-analysis.

The copper-based current collectors' performances highlight the benefit of incorporating oxygen and tin, also predicted from the meta-analysis (Fig. 3-17b). The copper foil cell was only

able to cycle 33 times with an average CE of 95.3%. The 3D structure of the CF appears to provide some benefit, increasing cycle life to 44, but resulted in a decrease in average CE to 94.3%. In contrast, the altered copper foams had much greater cycle life, with OCF reaching 72 cycles and SnCF achieving 83 cycles. CE was also improved, averaging 97.5% and 97.3% for OCF and SnCF respectively. The benefit of the addition of oxygen and tin is particularly obvious in the CE of the first 30 cycles (inset of Fig. 3-17b). The CEs of OCF and SnCF stabilized immediately, while an additional 6 and 5 cycles were needed for the copper foil and CF CE to stabilize. This observation supports the basis for oxygen and Sn inclusion noted in Section 3.4.2. A more stable SEI due to the increased presence of Li_2O or electronically insulative species originating from the incorporation of oxygen would reflect in quick stabilization of CE. Denser lithium plating and stripping influenced by the presence of Sn would have a similar effect.

To ensure reproducibility, four cells with each current collector were cycled and performance analyzed. The difference in performance between AC and CFP was significant across all cells (Fig. 3-18a-b and Table 3-12), but significant variation in performance metrics was observed within cells with the same current collector for the copper-based samples (Fig. 3-18c-f and Table 3-12). Statistical analysis was therefore employed to verify that the trends observed for the best performing cells hold across multiple experiments. ANOVA statistical analysis with a p-value of 0.05 confirmed statistically significant differences in average cycle life between all copper-based current collectors, with a test statistic of 0.038, and between the CF-based current collectors with a test statistic of 0.037.

Table 3-12: Average cycle life and CE of cells used for experimental validation. Four cells of each current collector vs. lithium were cycled and their performances are included in the averages.

	Current Collector	Average CE (%)	Average Cycle Life
Copper Base Material	Copper Foil	95.62±0.73	30±3
	CF	94.62±2.0	39±4
	OCF	97.48±0.17	55±11
	SnCF	97.10±0.14	68±18
Carbon Base Material	AC	88.51±5.0	53±13
	CFP	99.92±0.07	244±114

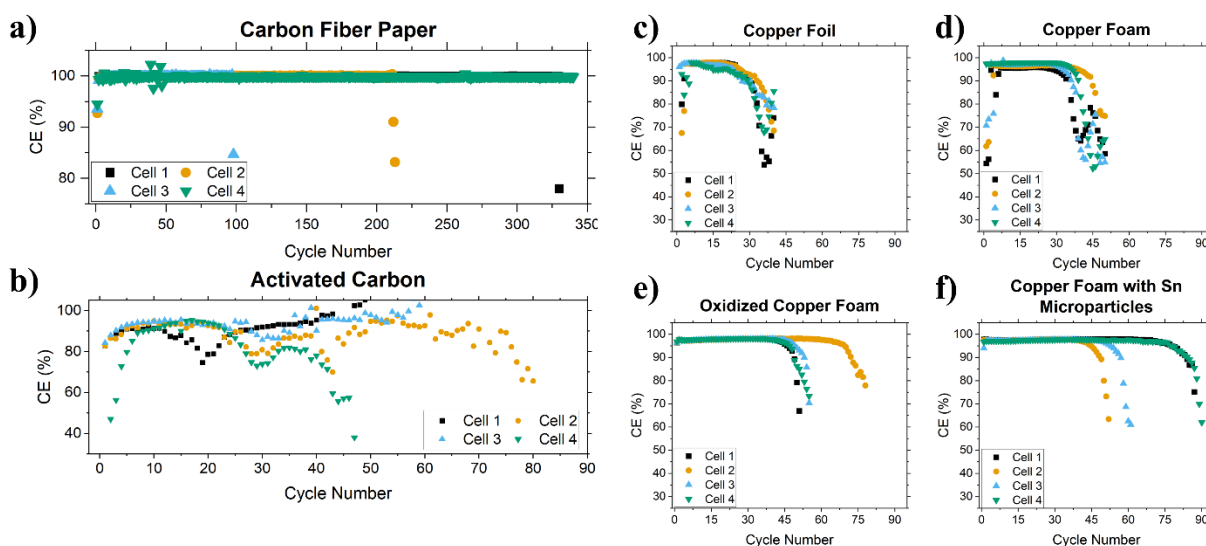


Figure 3-18: Performance of four cells with carbon-based current collectors of (a) carbon fiber papers and (b) activated carbon and of four cells each using copper-based current collectors of (a) foil, (b) foam, (c) oxidized foam, and (d) foam with Sn microparticles.

To extract where the statistical differences identified via ANOVA occur, Mann-Whitney U tests were employed (Table 3-13). As with the statistical testing in Section 3.2.3.2., the null

hypothesis assumes that the distribution of average cycle life or CE values for two different current collectors are not stochastically different. Once again, a p-value of 0.05 was set to determine significance. For the cycle life distributions, copper foil and CF are not statistically different, nor are OCF and SnCF. However, the distributions of copper foil and CF cycle life were all less than that of OCF and SnCF, verifying the benefit to cycle life of both oxygen and Sn. For CE, copper foil and CF were not different, and foil again had significantly lower CE than OCF and SnCF, as did foam compared to OCF. Unlike cycle life, the distribution of average CEs for SnCF was not significantly different than CF and was less than that of OCF. These results again likely relate to the impact of oxygen and Sn. A stable SEI consumes less lithium per cycle, increasing the average CE. Conversely, while alloying reactions lead to dense lithium morphology, there is a greater risk of losing active lithium to those alloying reactions. The SEI formed with the SnCF current collector is also not stabilized beyond the improved morphology and thus may still be fragile and continually reform and consume lithium, further reducing CE. Nonetheless, the experimental results align with what the meta-analysis predicted, resulting in better cycle life for both modified copper foams and higher CE for the OCF.

3.4. DISCUSSION AND IMPLICATIONS OF STUDY

Overall, the experimental results validate the conclusions from the machine-learning coupled meta-analysis, supporting the claim that such analysis can be used to gain important insight into material design. However, there are a few limitations to this study that should be acknowledged. Most crucially, it must be noted that CE and cycle life are not consistently reported in literature. Some reported CE values are averages over the reported cycle life while some are the CE of the cycle number reported as the end of cycle life. Likewise, there is no consistent definition for cycle life and end of life. As such, cycle life reports were observed to be the cycle

number at which a cell shorts or the cycle number at which the cell's CE drops below a certain percentage that frequently varied study to study. While we believe that the insights extracted in this meta-analysis are accurate despite the inconsistency in CE and cycle life reporting, the discrepancies would strongly impact predictive modeling. Examining the effect of these differences both on the modeling completed here and on predictive modeling is outside of the scope of the present work but could lead to interesting insights.

Additionally, there were many other aspects of both current collector properties and testing parameters that were not considered here to generate and maintain enough data after cleaning to allow for analysis. For example, pore volume was not considered as it is rarely reported. Separator material information was also collected, but limitations due to inadequate details provided or the use of discontinued products without descriptions of the material lead us to remove those features from analysis. Similarly, many experimental conditions are unintentionally excluded from reporting, including spring type, spacer thickness, and crimping pressure among others, though recent literature indicates that these factors have an effect on cell performance.¹⁷⁷ There is likely valuable information and insights to be found from analyzing performance while accounting for these features. However, with the current body of literature, it would be extremely difficult to gather sufficient and quality data.

While the goal of this work was not to design the optimal 3D current collector, the insights gained from this and similar meta-analyses could be used for this aim, again if the quantity and quality of data is sufficient. It is vital for publications to include as much and as detailed experimental information as possible to enable the most accurate insight from the tools now available to draw conclusions from large amounts of data.

3.5. SUMMARY

In conclusion, a meta-analysis employing data science and machine learning was undertaken to extract key properties of 3D current collectors for lithium metal anodes. A moderate specific surface area of 0.01-100 m²/g and the inclusion of oxygen and tin were revealed to correlate to high cycle life and CE. Experimental validation confirmed these insights, with a carbon fiber current collector with a moderate specific surface area vastly outperforming an activated carbon current collector with an extremely high specific surface area. Similarly, copper foam current collectors modified with oxygen and with tin microparticles displaying greater cycle life and CE than copper foil and unalter copper foam. This study exhibits how meta-analysis coupled with machine learning can be used to extract trends from a large volume of data and thus guide informed material design. As machine learning tools become more widely available, these analyses can provide important insight into battery electrode design and accelerate advances in the field.

Chapter 4. Deconvoluting the Impact of Current Collector Structure and Electrolyte Selection on Coulombic Efficiency of Lithium Metal Anodes

4.1. INTRODUCTION

4.1.1. *Realistic LMB Design and Operation*

As analyzed in Chapter 3, there is an expansive volume of work on 3D current collectors for lithium metal batteries and anodes. Despite this large body of literature, there is no clear consensus on whether 3D current collectors improve performance in cells under realistic operating conditions. Published studies typically assess performance in half cells of lithium vs. the current collector of interest, as was examined in Chapter 3, or symmetric cells, where meaningful CE measurements cannot be attained. When full cell results are included, the cathode loading is frequently on the order of 0.25-2 mAh/cm² which is much less than the standard 4 mAh/cm² or higher loading required for high energy density applications. Additionally, reported full cell results often are from anode-free cell configurations and rely on the cathode to supply all lithium in the cell. However, it is widely acknowledged that anode-free configurations are far from practical application and that a lithium reservoir is required to enable acceptable cycling and efficiency, as outlined in Section 1.3.1.¹⁰ As such, there is a large gap in knowledge of how 3D current collectors impact anode cycling performance when a lithium reservoir is present.

In addition to the absence of investigation into current collector performance with a lithium reservoir present, to the best of the authors' knowledge, there are almost no studies examining the effect of electrolyte formulation as well as current collector on performance. There have been many advances in electrolyte for LMBs in recent years, but little work examining the intersection of electrolyte and current collector structure choice. Electrolyte formulation has been systematically shown to have significant effect on lithium morphology, SEI composition and

properties, and LMA cyclability, as noted in Section 1.3.3. However, electrolyte properties such as ionic conductivity and the process of SEI formation and SEI properties could have greater impacts on performance when a 3D current collector is present. Ionic conductivity dictates Li-ion concentration gradients in the electrolyte, which could be much more consequential through the free volume of a 3D current collector than at the surface of planar 2D current collector or lithium reservoir. Similarly, greater surface area of plated lithium on a 3D structure could result in more SEI formation than a 2D surface. These interacting factors have not been analyzed to our knowledge.

4.1.2. Coulombic Efficiency Measurements

While CE is a common performance metric for both half-cells and full-cells, the accuracy and relevance of the measurement can vary widely depending on the testing method utilized. Very often, to evaluate a substrate's efficiency in plating and stripping lithium, the simple plating and stripping protocol analyzed and employed in Chapter 3 is considered sufficient. However, this method mimics anode-free cycling, which was noted as inefficient for realistic applications. It may also be misleading as different side reactions may occur at the surface of the substrate than would occur on the surface of pure lithium. Some researchers address this issue by conducting symmetric cell tests, placing two lithium reservoirs against each other and plating and stripping a set capacity between the two. While important polarization and impedance data may be gathered this way, any CE reported from symmetric cell testing is highly misleading as the cycling is controlled by capacity, the same metric used to determine CE. Disregarding small variations from battery cycler measurement error, the CE should always be 100% in symmetric cell testing if equivalent capacity is being cycled between the lithium electrodes.

Though standard half-cell and symmetric cell testing is inadequate for CE testing, a method is still needed to determine CE when a lithium reservoir is present. Luckily, such methods have been developed. The Aurbach group at Bar-Ilan University first reported a method in 1989 to extract a physically significant CE in a half-cell format.^{178,179} Their protocol consisted of the plating a reservoir of lithium onto a substrate, plating and stripping a fraction of that lithium in “shallow cycles”, and finally stripping all remaining lithium from the substrate. Their CE calculation considers all the lithium plated and stripped during the test, determining an average CE of all cycles as:

$$CE_{avg}(\%) = \frac{n*Q_C + Q_S}{n*Q_C + Q_T} * 100 . \quad \text{Eq. 4-1}$$

where Q_T is the capacity of the lithium reservoir, n is the number of shallow cycles, Q_C is the capacity of the shallow cycles, and Q_S is the capacity of the final strip.

Researchers from Pacific Northwest National Laboratory (PNNL) revisited the protocol in 2018 when investigating CE testing in half-cells and proposed the addition of a formation cycle to stabilize the SEI and obtain more consistent CE values.¹⁸⁰ The formation cycle recommended was deep plating and full stripping of the desired reservoir capacity, repeated until the CE of the formation cycles stabilized. The use of this modified Aurbach protocol has increased in the years since the study was published, with many researchers utilizing it to exhibit electrolyte performance, typically employing one formation cycle and 10 shallow cycles.^{19,22,181} These methods guided experiments in this work and allowed for meaningful comparison between 3D current collectors and electrolyte formulations.

4.1.3. *Summary of Work*

Overall, despite large advances in performance realized by developing new electrolytes, the relative weight of benefit provided by optimization of electrolyte has not been compared to the

benefit of the use of 3D current collectors. To our knowledge, no work has been published within this area. Liu et. al. systematically analyzed carbon electrodes of varied structure in different electrolytes in 2021, but no similar work has been done with significant lithium reservoirs.¹⁸² Thus, the practical benefits of these current collectors in application-relevant configurations remain uncertain, as does their relative importance for LMA performance compared to electrolyte formulation.

This work aims to elucidate the effect of 3D current collectors and electrolyte selection for realistic LMAs. Four commercially available current collectors - copper foil, copper foam, copper mesh, and copper mesh layered on copper foil - were tested using a protocol designed to mimic full-cell cycling while isolating the anode, to determine if any current collector structure improves performance. To account for potential interactions between structure and electrolyte, the current collectors were paired with four electrolytes at different stages of application. Coulombic efficiency (CE) testing emulating lithium cycling from a lithium reservoir showed no significant variation when current collector was changed and electrolyte held constant. However, significant differences were observed when comparing cells with the same current collector but different electrolytes. While polarization and electrochemical impedance measurements correlated with the morphology of cycled lithium in the cells, these differences did not correspond to variation in CE values. These data indicate that electrolyte selection plays a much larger role in cell performance than the choice of current collector structure. Consequently, efforts to improve cell performance and design should prioritize electrolyte optimization.

4.2. METHODS

4.2.1. Current Collector Selection and Preparation

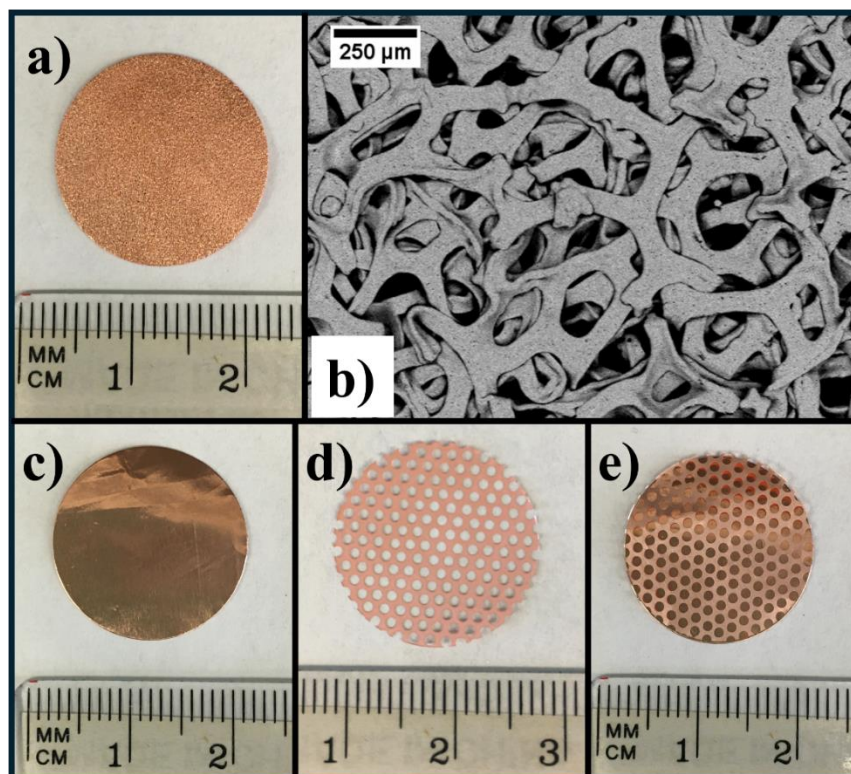


Figure 4-1: Copper current collectors consisting of a,b) a copper foam 100 μm thick with pores on the order of 30-200 μm in diameter, c) a 12 μm thick copper foil, d) a 9 μm thick copper foil with 1mm diameter punched holes (referred to as “mesh”), and e) a composite structure of 9 μm thick mesh layered on top of 12 μm foil, were tested. The mesh had a matte (d) and reflective (e) side, and the reflective side was always placed facing lithium during cell assembly.

Four commercially available copper current collectors with different structures were chosen for testing. These included a 100 μm thick copper foam (Fig. 4-1a-b), a 12 μm thick copper foil (Fig. 4-1c), a 9 μm thick copper foil with 1mm diameter punched holes (hereafter referred to as mesh) (Fig. 4-1d), and a composite structure of the mesh layered on top of the foil (Fig. 4-1e). All copper current collectors were purchased from MTI Corporation. To remove surface oxidation

and impurities, each current collector was treated by immersion in 1M hydrochloric acid for 15 seconds, followed by triple rinsed in deionized water and ethanol, and then dried overnight in a vacuum oven.

4.2.2. *Electrolyte Preparation*

Four electrolytes were chosen for testing to represent both the commonly used formulations in literature and recent state-of-the-art advances. An ether-based electrolyte composed of 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1:1 vol/vol dimethoxyethane (DME) and dioxolane (DOL) with 0.3M LiNO₃ additive served as the literature baseline electrolyte, referred to here as LiTFSI, that is frequently used in half cell testing (Gotion, Inc.). A 1:1.2:3 mol:mol mixture of lithium bis(fluorosulfonyl)imide (LiFSI) (Nippon Shokubai) with DME (Gotion, Inc.) and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (TTE) (Synquest Laboratories, Inc.), known as M47, was used as a well-studied state-of-the-art electrolyte. Finally, two additional state-of-the-art electrolytes (abbreviated F4 and F5) were tested, consisting of 1.2M LiFSI in 1,2-bis(2,2-difluoroethoxy)ethane (F4DEE) and 1.2M LiFSI in 2-[2-(2,2-difluoroethoxy)ethoxy]-1,1,1-trifluoroethane (F5DEE) respectively. F4DEE and F5DEE were provided by collaborators from Stanford University.¹⁹ All solvents were dried using molecular sieves for at least 7 days prior to use. The acronyms for these electrolytes are shown in Table 4-1.

Table 4-1: Acronyms for electrolytes used in study.

Electrolyte Acronym	Electrolyte Formulation
LiTFSI	1M LiTFSI in 1:1 vol/vol DOL:DME with 0.3M LiNO ₃
M47	1:1.2:3 mol:mol LiFSI:DME:TTE
F4	1.2M LiFSI in F4DEE
F5	1.2M LiFSI in F5DEE

4.2.3. *Electrochemical Testing*

4.2.3.1. *Cell Configuration*

All electrochemical cycling experiments were conducted using 2032 coin cells. The cells were assembled in an argon glovebox (Vacuum Technologies, Inc.) with an oxygen and water concentration maintained below 0.01 ppm. For assembly, the copper current collector was placed counter to a 250 μm thick lithium chip, and 60 μL of electrolyte was added to each cell. For the LiTFSI and M47 electrolytes, a 16 μm thick polyethylene separator (Nanoshel LLC) was used while Celgard 2325 separator was used for F4 and F5. The separator that resulted in the best performance was chosen for each electrolyte to ensure ideal cycling was compared.

4.2.3.2. *Coulombic Efficiency Measurement*

To accurately and meaningfully measure performance differences for the current collector|electrolyte combinations, the modified Aurbach protocol developed at PNNL was chosen as the CE determination method. The number of formation cycles and number of shallow cycles were altered from their original work to clearly extract differences between cells. The adequate number of formation cycles needed to be determined due to the varied current collectors. Half-cells of each current collector and electrolyte combination were assembled as described in Section 4.2.3.1. Four mAh/cm² of lithium was repeatedly plated onto the structure at 0.4 mA/cm² and stripped at the same current density to 1V (Fig. 4-2). The greatest number of cycles required for the CE to stabilize under these conditions for a current collector|electrolyte pairing was found to be 8 cycles, and thus 8 formation cycles were performed for all testing. Additionally, the number of shallow cycles was altered from the typical 10 cycles to examine changes in voltage polarization, electrochemical impedance, and morphology over time. One hundred and fifty cycles were selected to balance cycling time yet allow enough cycles to exhibit changes in the relevant

properties. The current density was selected to mirror C/10 cycling in a full cell with a 4 mAh/cm² cathode, a typical loading for lithium nickel manganese cobalt oxide cathodes in high energy density LMBs. As the focus of the study revolves around the thermodynamic behavior of the lithium anode and electrolyte, higher current density to evaluate kinetics were not included. An example time vs. voltage profile is shown in Fig. 4-3a. All cells were held at 25°C during testing. For each combination of current collector and electrolyte, three cells were cycled. The average and range of values are reported to ensure accuracy and reproducibility.

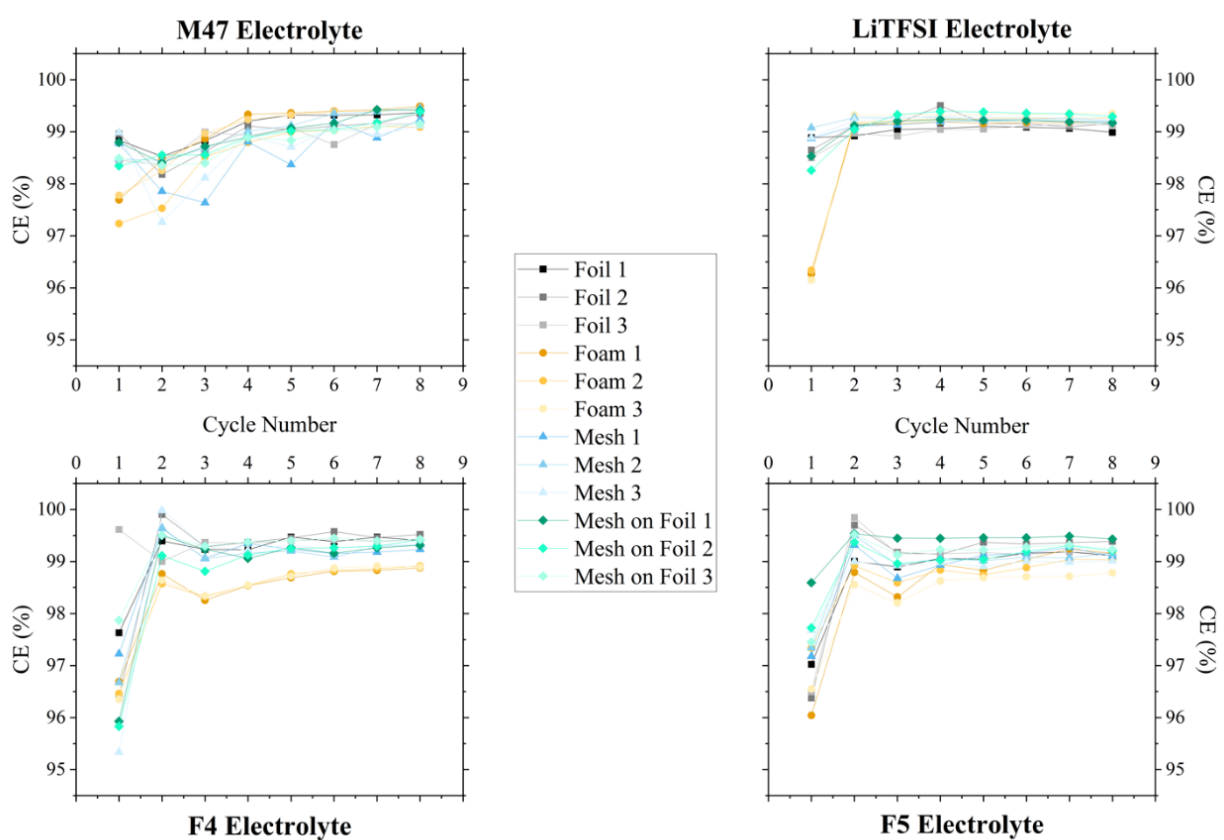


Figure 4-2: Coulombic efficiency (CE) of half cells of each current collector|electrolyte combination undergoing repeat plating and stripping to 1V of 4mAh/cm² of lithium at 0.4 mA/cm² to determine an appropriate number of formation cycles.

4.2.3.3. *Electrochemical Impedance Spectroscopy*

Electrochemical impedance spectroscopy (EIS) measurement was conducted using a Gamry potentiostat at four stages of cycling process: 1) after completing the 8 formation cycles and deposition of the lithium reservoir; 2) after 20 shallow cycles; 3) after 100 shallow cycles; and 4) after 150 shallow cycles, immediately before the final stripping step. Spectra were measured over a frequency range of 1MHz to 0.5 Hz, at 10mV with 10 points per decade. The measured spectra were fitted to a model circuit using the impedance.py package in Python.¹⁸³

4.2.4. *Morphology Characterization*

Focused ion beam (FIB) milling and secondary electron microscopy imaging were conducted using a Thermo Scientific Aquilos 2 Cryo-FIB SEM. After cycling, cells were disassembled in an argon glovebox. The copper current collector with lithium was rinsed with DME for cells containing LiTFSI and M47 electrolyte, and with their respective solvents for cells with F4 and F5 electrolyte. The current collectors were then dried under vacuum in the glovebox antechamber for at least 15 minutes. Samples were mounted at room temperature in the glovebox using silver paste (Ted Pella, Inc.), sealed under argon for transit to the SEM, transferred into the SEM chamber under vacuum, and cooled to cryogenic temperatures in the SEM chamber. To image cross sections, the lithium was first rough milled at 30 nA and 7 nA, then cleaned with a 1 nA ion beam. Cross sectional images were taken at a 28° stage tilt, and both surface and cross-sectional images were obtained using a 10 kV electron beam acceleration.

4.3. RESULTS AND DISCUSSION

4.3.1. Coulombic Efficiency

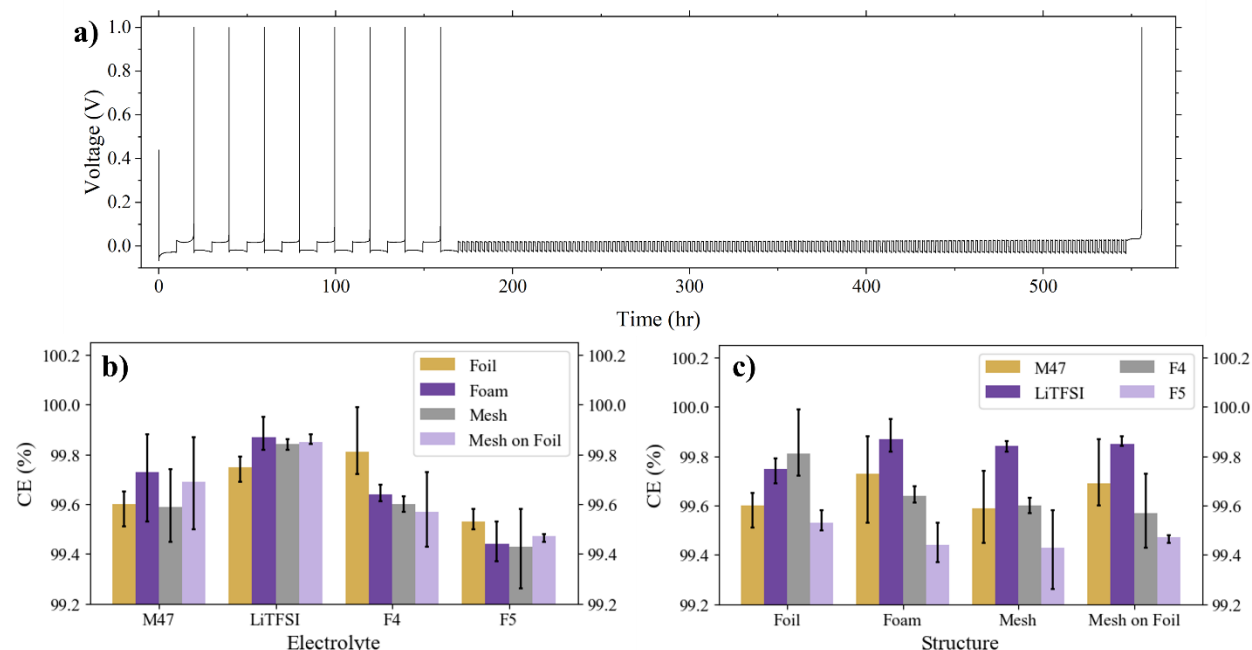


Figure 4-3: Coulombic efficiency (CE) measurements of different current collector/electrolyte combinations. The measurement consisted of a) deep plating and stripping formation cycles followed by repeated plating and stripping of a fraction of a lithium reservoir, as shown in an example voltage vs. time curve. The results are shown two ways: b) grouped by electrolyte with varying current collector, and c) grouped by current collector, with varying electrolyte. Error bars show the range of CE values, with the ends at the maximum and minimum values measured.

To evaluate the performance of various current collector structures under conditions analogous to full-cell cycling while isolating the anode, CE was calculated as described in section 4.2.3.2. A typical voltage vs. time curve observed during cycling is shown in Figure 1a. The aim of the protocol is to mimic cycling of the LMA in a full-cell with a lithium reservoir, which is currently a necessity for enabling long cycle life in high energy density batteries. The four current collectors (Fig. 4-1) were paired with the four electrolytes for a total of sixteen combinations, and

three cells were tested per combination. The average of the triplicates' average CE measured for each combination are listed in Table 4-2. The average CEs with the range of measured values indicated by errors bars are presented in Fig. 4-3b as grouped by electrolyte. Within each electrolyte group, there is no significant difference in average CE as the range in CE values obtained in testing overlaps with two exceptions. The foil current collector cycled with F4 provides higher CE than the foam and mesh but not the layered mesh on foil. In the LiTFSI electrolyte group, foil shows a lower average CE than the other current collectors.

Table 4-2: Measured average CE values of three cells of each combination of current collector and electrolyte.

M47		LiTFSI		F4		F5	
Substrate	CE (%)	Substrate	CE (%)	Substrate	CE (%)	Substrate	CE (%)
Foil	99.60	Foil	99.75	Foil	99.81	Foil	99.53
Foam	99.73	Foam	99.87	Foam	99.64	Foam	99.44
Mesh	99.59	Mesh	99.84	Mesh	99.60	Mesh	99.43
Mesh on Foil	99.69	Mesh on Foil	99.85	Mesh on Foil	99.50	Mesh on Foil	99.47

When the CE results are plotted as grouped by current collector (Fig. 4-3c), however, there are clear differences in average CE when different electrolytes are used. For the foil current collector, the LiTFSI and F4 electrolytes demonstrated higher CE than the M47 and F5 electrolyte cells. The combination of LiTFSI electrolyte and foam outperformed the F4 and F5 electrolytes, as did the combination of LiTFSI electrolyte and layered mesh on foil. The LiTFSI electrolyte also provided higher CE when using the mesh current collector than any of the other electrolytes.

As stated above, the error bars in Fig. 4-3b-c report the range in average CE values measured. The error was presented as such due to the small sample size. While standard deviation is typically calculated to show variance, smaller sample sizes render it misleading. Variance could

arise from a variety of causes, including internal cell pressure distribution differences, electrolyte wetting behavior, electrolyte quality, or simply from the inherent inconsistencies of human assembly of coin cells. Differences in pressure distribution or electrolyte wetting behavior originating from current collector structure would most probably result in similar magnitudes of error for each current collector regardless of electrolyte type. Similarly, electrolyte wetting behavior differences between electrolyte formulations would appear as similar ranges within electrolyte groupings. However, the magnitude of the range of measured values within each electrolyte grouping as well as within each structure grouping is not consistent. The inconsistency indicates that the variation originates from random error such as human error in cell assembly rather than systemic error. While the ranges in CE could complicate analysis of performance, statistical tools provide robust methods to enable evaluation.

Table 4-3: Summary of ANOVA statistical testing of average CE values.

Null Hypothesis: The means of each group are equal. Reject if ANOVA F statistic > 3.24 (equivalent $\alpha > 0.05$)				
Consistent Variable		Changed Variable	F Statistic	Reject H_0 ?
Electrolyte	M47	Current Collector	0.399	Fail to Reject
	LiTFSI	Current Collector	2.345	Fail to Reject
	F4	Current Collector	2.759	Fail to Reject
	F5	Current Collector	0.284	Fail to Reject
Structure	Foil	Electrolyte	5.693	Reject
	Foam	Electrolyte	7.546	Reject
	Mesh	Electrolyte	7.094	Reject
	Mesh on Foil	Electrolyte	7.060	Reject

Statistical analysis of the data using the Analysis of Variance (ANOVA) method supports the greater impact of electrolyte observed while also accounting for the range in measured CE

values. The mean average CE of each combination was compared to the means of the other combinations containing consistent electrolyte. Every mean CE was also compared to the means of combinations with consistent current collector. The null hypothesis assumes that all means are equal, and an alpha value of 0.05, equivalent to an F value of 3.24, is the threshold for rejection. The results of the analysis are shown in Table 4-3. When the electrolyte was consistent, the means of each current collector are not statistically significantly different. However, when the current collector was consistent and electrolyte is changed, there is a statistically significant difference in the means. These conclusions hold for every case tested, further confirming that current collector structure is inconsequential compared to electrolyte choice.

From the CE data reported, the ideal electrolyte for each current collector is as follows: F4 (foil); LiTFSI, F4, or F5 (foam); LiTFSI (mesh); and LiTFSI or M47 (mesh on foil). The LiTFSI electrolyte demonstrates high CE with each current collector apart from foil. This is not unexpected. The CE calculation in Equation 1 indicates the efficiency of lithium metal utilization within electrolytes under low and limited voltage ranges. However, battery cyclers measure capacity based on electron consumption, which includes contribution from lithium plating and SEI formation. Consequently, an electrolyte that forms less SEI will yield a higher CE, as calculated by Equation 1, as a greater portion of electrons are used for lithium plating rather than SEI formation. LiTFSI is known to be stable against pure lithium and allow repeat stripping and plating with minimal SEI build-up.¹⁸⁴ It is important to reiterate the limited and low voltage range at which half-cell CE measurements are conducted. While these tests provide valuable insights into electrolyte compatibility with the anode, they cannot predict electrolyte behavior in the presence of cathode materials under an expanded voltage window. For example, although the LiTFSI electrolyte exhibits high performance in this study, it is known to be unstable at high voltages and

demonstrates significantly poor cyclability in full-cell configurations compared to the M47, F4, and F5 electrolytes.

4.3.2. Polarization

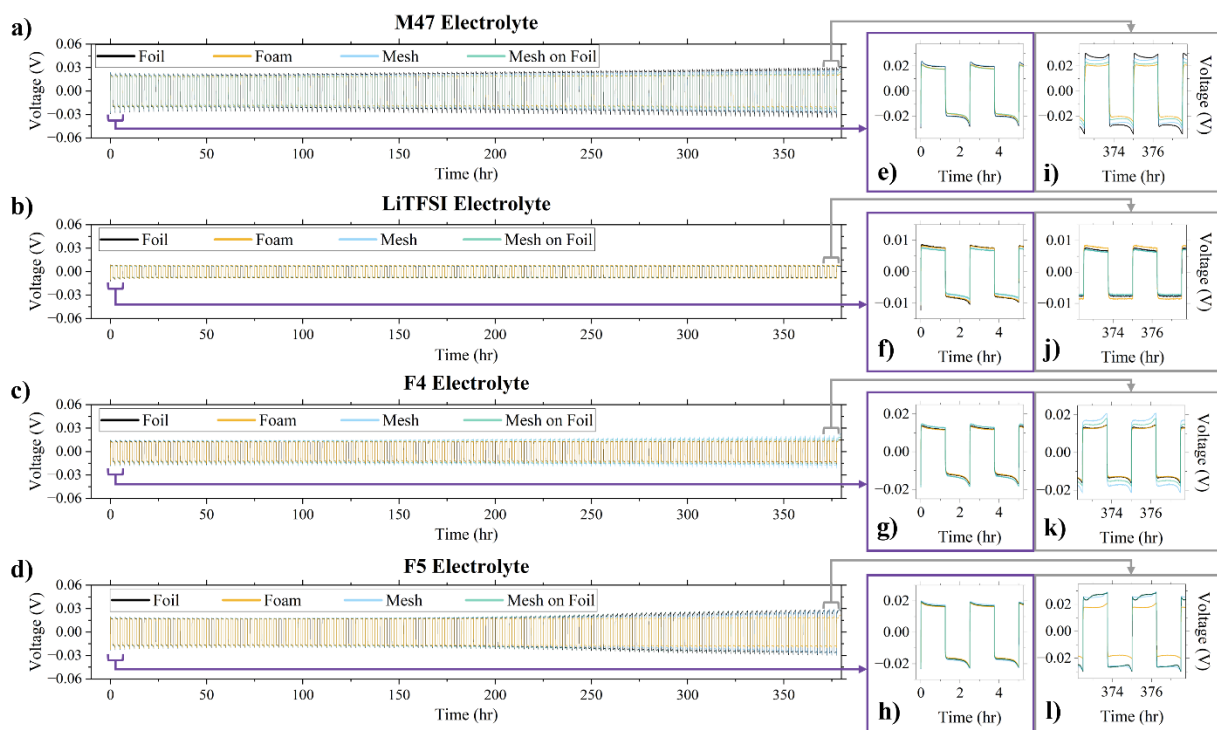


Figure 4-4: Voltage vs Time curves visualize polarization during shallow cycling of each current collector paired with a) M47, b) LiTFSI, c) F4, and d) F5 electrolyte. Insets magnify the first two cycles (e-h) and the last two cycles (i-l) for each current collector in the respective electrolytes.

To elucidate differences in cycling and electrochemical behavior that convoluted by average CE, voltage polarization of each current collector/electrolyte combination during shallow cycling was analyzed (Fig. 4-4). The term polarization in this discussion is any deviation of voltage from zero when current is applied. Additionally, plating and stripping in this discussion are in reference to the current collector with the deposited lithium reservoir, not the lithium chip. Gradual increases in both plating and stripping polarization occurred over shallow cycling for the

foil and mesh in M47 electrolyte (Fig. 4-4a), for the mesh and mesh on foil in F4 electrolyte (Fig. 4-4c), and for all current collectors apart from the foam for the F5 electrolyte cells (Fig. 4-4d). For all current collectors in the LiTFSI electrolyte, the polarization remained constant, even slightly decreased over cycling (Fig. 4-4b).

The initial and final short cycles are plotted to further investigate differences in polarization (Fig. 4-4e-l). No difference in polarization magnitude nor shape is observed in the first two cycles between current collectors in the same electrolyte (Fig. 4-4e-h). The voltage curve shape is also consistent across electrolytes. Slight differences in magnitude of polarization between electrolytes are present however, with extremes of 8.3 mV for LiTFSI and 20 mV for M47. These differences likely originate from two sources: differences in ionic conductivity between electrolytes, and resistivity of the SEI. While low polarization is frequently used to claim long cycle life, researchers also conclude that a more electrically resistive SEI improves battery performance.¹⁸⁵ Increased electrical resistance limits side reactions at the interface that reduce CE and consume electrolyte compounds and lithium. A more resistive SEI may have contributed to the increased magnitude of polarization in the M47, F4, and F5 electrolytes (20, 12, and 19 mV when stripping lithium compared to 8.3 mV for LiTFSI). As such, greater magnitude of polarization is not considered detrimental to performance.

Additionally, across all cells, the stripping (positive voltage) and plating (negative voltage) curves are not symmetrical in shape nor magnitude. For example, in the first cycle the foil|F4 cell demonstrated a maximum stripping voltage of 12 mV and a minimum plating voltage of -17 mV. As polarization of a two-electrode cell is a combination of two interfaces, one at which lithium is stripped and one at which it is plated, the precise origins of these differences cannot be identified.

However, the asymmetry in the voltage curves can be assumed to arise from asymmetric kinetics of the processes of plating and stripping.^{186,187}

By the 149th and 150th cycles, the voltage curve shape varies more widely both between electrolytes and between current collectors (Fig. 4-4i-l). In the M47 electrolyte, all voltage curves shifted similarly to a flatten U-shape, where the polarization at the beginning and end of the plating and stripping processes are greater than in the middle of the process (Fig. 4-4i). These differences without changes in current indicate slower kinetics at the beginning and end of the half cycles compared to the rest of the cycle. The shape is most pronounced for the foil current collector. The peak at the end of plating is of larger magnitude than the peaks during stripping, similar to the first cycles, with voltages of -34 mV and 29 mV recorded respectively. While all current collectors' polarizations demonstrate a similar shape, total overpotential, the difference between the minimum and maximum voltage recorded in one plating/stripping cycle is greatest for the foil (63 mV) and least for the foam (45 mV). Despite the lower magnitude of overpotential observed for the foam, the average CE was not significantly different between it and the foil (Fig. 1a), and none of the M47 combinations show significantly different CEs.

The voltage curves at the end of shallow cycling for the F4 electrolyte cells also demonstrate a slight U-shape, though with less difference between extreme values in comparison to the M47 cells (Fig. 4-4k). The differences in kinetics at the onset and end of cycling are not as large as in the M47 electrolyte. The foil and foam have nearly the same total polarization magnitude (31 and 29 mV) as the initial cycles (29 mV and 28 mV). The mesh overpotential increased at later cycles from a total of 32 mV in the first cycle to 42 mV in the last. Interestingly, the similarity in polarization for the foil and foam did not translate to similar CEs, with the foil being the one current collector with significantly higher CE than both the foam and mesh in F4

(99.81% compared to 99.64% and 99.60% respectively) (Fig. 4-3a). Similarly, the differences in the polarization between the foam and mesh cells did not correspond to differences in CE.

The F5 electrolyte combinations exhibited the greatest change in polarization in late cycling with the exception of the foam current collector (Fig. 4-4l). The total overpotential increased from 41 to 58 mV for the foil, from 42 to 59 mV for the mesh, and from 42 to 58 mV for the layered mesh on foil. The foam and mesh have very similar voltage curves to the F4 cells. Conversely, the foil and mesh on foil in the F5 electrolyte exhibit a unique voltage curve, involving an initial U-shape as noted in other samples, followed by a plateau. The plating voltage curves are a mirror image of the stripping, beginning with a plateau, then forming a “U” to an absolute maximum at the end of plating. The origin of this unique curve is not clear and is outside of the scope of this study. However, once again, a correlation with overpotential magnitude or voltage curve shape with CE does not appear.

Compared to the other electrolytes, the current collectors in the LiTFSI electrolyte have consistent voltage curves throughout cycling. The stripping voltage curves of the 149th and 150th cycles are nearly identical to those of the 1st and 2nd cycles, with a slight decrease in the magnitude of total overpotential. The total overpotential dropped from 19 to 15mV (foil), from 17 to 16mV (foam), from 16 to 14 mV (mesh), and from 16 to 14 mV (mesh on foil). The later cycle plating voltage curves are flatter than the early cycle curves, the voltage remaining nearly constant throughout the plating process. Once more, no correlation between overpotential and CE appears between the combinations using LiTFSI electrolyte.

4.3.3. *Electrochemical Impedance Spectroscopy*

To further investigate the changes observed in the polarization and electrochemical differences, electrochemical impedance spectroscopy (EIS) was performed on each combination

after the initial reservoir plating and after 20, 100 and 150 shallow cycles were completed (Fig. 4-5 and 4-6). Spectra typically measured an offset semi-circle at frequencies of 1-10kHz, followed by a linear feature from 1-100Hz, and a linear diffusion tail at low frequencies (Fig. 4-5a). The python package impedance.py was used to fit the spectra to a model circuit focused on the elements from 1MHz to 1kHz, namely the bulk resistance (R_{bulk}) and interfacial resistance (R_{I})(Fig. 4-5b-e). R_{bulk} includes the electrical and ionic resistance of all components of the cell while R_{I} , fitted to the feature at 1-10kHz, corresponds to the resistance at the electrode|electrolyte interfaces.^{188–}

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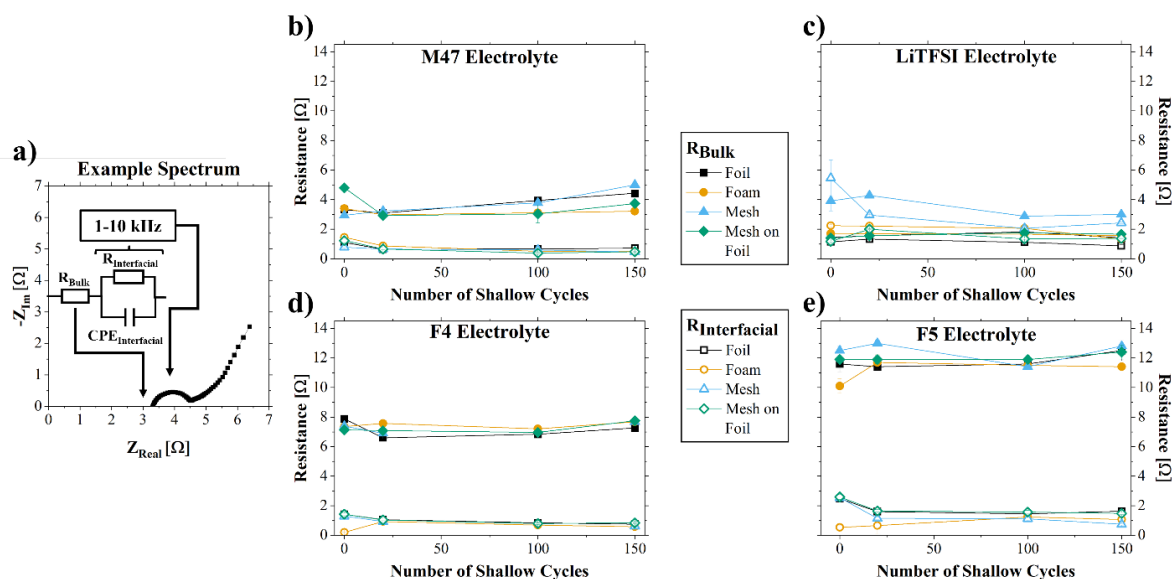


Figure 4-5: Electrochemical impedance spectra were fit with the equivalent circuit shown (a). The resistances determined by fitting are plotted for each current collector paired with b) M47, c) LiTFSI, d) F4, and e) F5 electrolyte. Solid filled symbols represent the fitted bulk resistance, and hollow symbols represent the interfacial resistance.

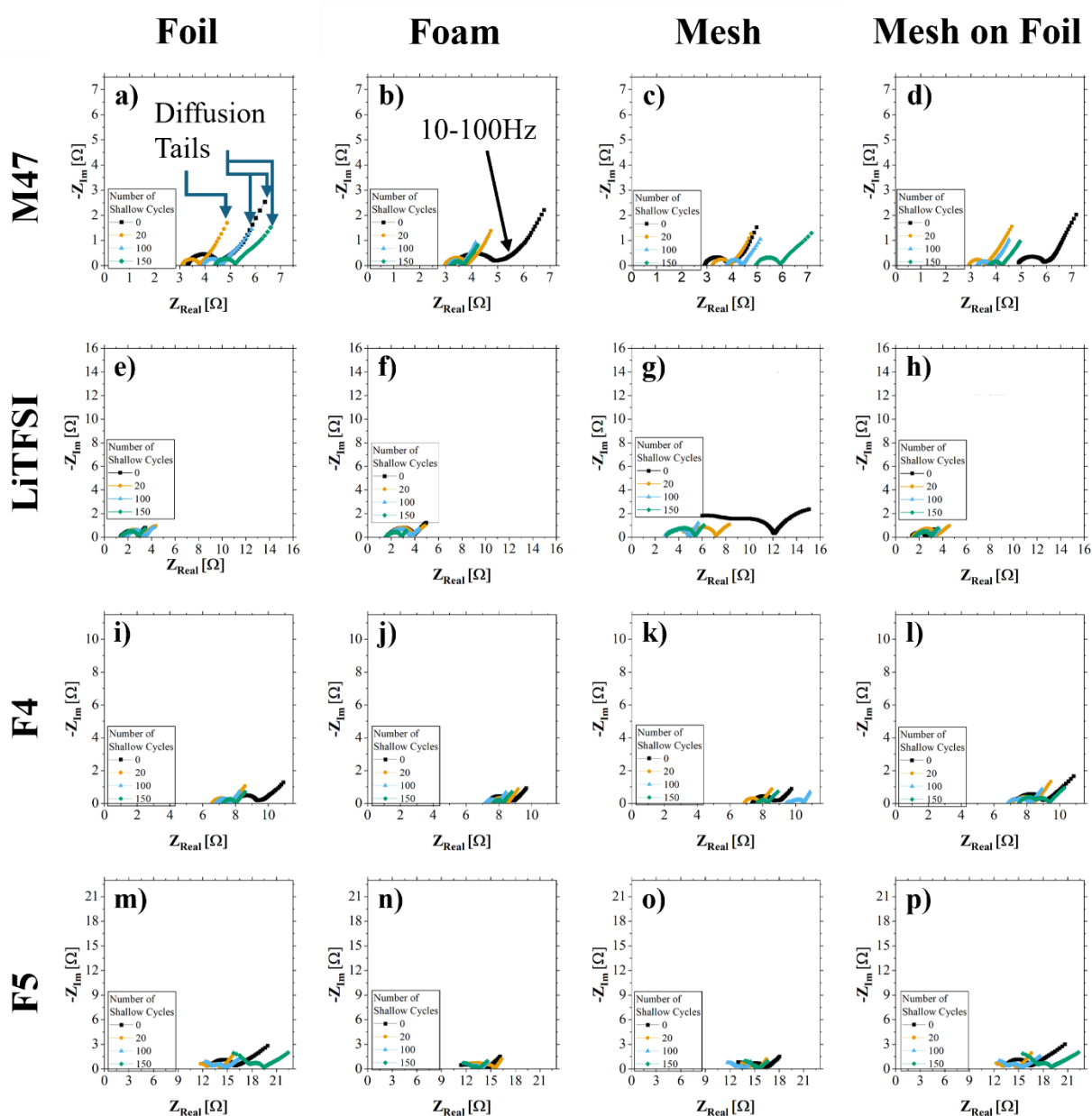


Figure 4-6: Electrochemical impedance spectra of half cells of each current collector and electrolyte combination utilizing M47 (a-d), LiTFSI (e-h), F4 (i-l), and F5 (m-p) electrolyte, were measured after completing the formation cycles and the initial lithium reservoir deposition (0 shallow cycles, black), and after completion of 20 (gold), 100 (blue), and 150 (green) shallow cycles.

The greatest difference between electrolytes is seen in R_{bulk} (Fig. 4-5b-e). Large differences in R_{bulk} are likely due to different ionic conductivities between electrolytes, as well as differences in the resistivity of the SEI. The magnitude in R_{bulk} is not directly related to the overpotentials observed in the voltage curves. Though the LiTFSI cells show both the lowest R_{bulk} and overpotential, the M47, F4, and F5 recorded similar overpotential values in initial cycles. The lack of correlation between the two measurements may be due to the low current density employed during cycling obscuring effects of the electrolyte conductivity. The evolution of R_{bulk} also does not exactly mirror the evolution of overpotential observed. The foam in all electrolytes and all current collectors in LiTFSI exhibit mostly consistent R_{bulk} . As noted in section 4.3.2., the foam showed the least increase in overpotential over cycling for all electrolyte combinations, and all current collectors in LiTFSI had consistent or slightly reduced overpotential. Other combinations such as the foil and the mesh in M47, the mesh and layered mesh on foil in F4, and foil, mesh, and layered mesh on foil in F5, measured increases in both R_{bulk} and overpotential during cycling, though not as proportional magnitudes. Additionally, the foil paired with F4 and layered mesh and foil paired with M47 recorded opposite trends in R_{bulk} , which slightly decreased over cycling, and overpotential, which increased.

When interpreting EIS data, increases in bulk resistance in LMBs are often attributed to increases in surface resistivity from build-up of resistive SEI. However, the interfacial resistivity measurements observed here do not support this, remaining constant or even decreasing slightly over cycling for each combination. Therefore, slower processes are likely contributing to the increased polarization. Some combinations' spectra, particularly in the M47 electrolyte, have an additional feature at approximately 10-100Hz (Fig. 4-6a-d) a frequency often attributed to charge transfer kinetics.¹⁹⁰ Increases in the resistance of this feature could indicate a reduction of active

area for reaction due to ionic resistive phases forming on the surface or to the presence of dead lithium. In symmetric cells, it is a very difficult feature to fit and deconvolute due to the impact of two electrodes with significant and similar interfacial impedances. In almost every spectrum acquired, this feature blends into the diffusion tail and cannot be accurately quantified (Fig. 4-6). The spectra of the foil and the mesh in M47 electrolyte do exhibit this feature distinctly (Fig. 4-6a and c) and record an increase in diameter over cycling, supporting the idea that charge transfer kinetics are driving increased polarization.

R_{bulk} and polarization could also be affected by changes in diffusion rates, either within the electrodes or within the electrolyte. The EIS spectra exhibit slight differences in diffusion tails over cycling for all combinations that showed increased polarization and R_{bulk} . For the combinations that did not have any increase, the diffusion tails appear consistent. The discrepancies in the magnitude and sign of R_{bulk} changes when compared to polarization may be due to differences in diffusion behavior. However, these differences cannot be deconvoluted from the data here and may be worth additional study.

4.3.4. *Cryo-FIB-SEM*

To gain insight into the morphology of the cycled lithium, cryo-FIB-SEM images were taken of each current collector|electrolyte combination at the completion of shallow cycling (Fig. 4-7 and 4-8). The surfaces of the cycled lithium exhibit interesting elements. With the cells using M47 electrolyte, the foil has the flattest, largest grains (Fig. 4-7a) while the foam appears the most porous (Fig. 4-7b). The mesh and mesh on foil are very similar, with smaller lithium grains interspersed with small pores (Fig. 4-7c-d). All current collectors in the LiTFSI electrolyte have large lithium grains and appear dense, though more areas of insulative material appear as bright white charged spots than in the other electrolytes (Fig. 4-7e-h). The morphology of the lithium

in F4 (Fig. 4-7i-l) and F5 (Fig. 4-7m-p) electrolyte appear very similar from the surface, with smaller grains and tiny pores where they meet. The foam and mesh on foil in F4 have slightly larger grains that appear to have aggregated. Also of note, the surfaces of the foil and mesh on foil in F5 lithium are not noticeably different than the foam and mesh, though the polarization curves were distinct.

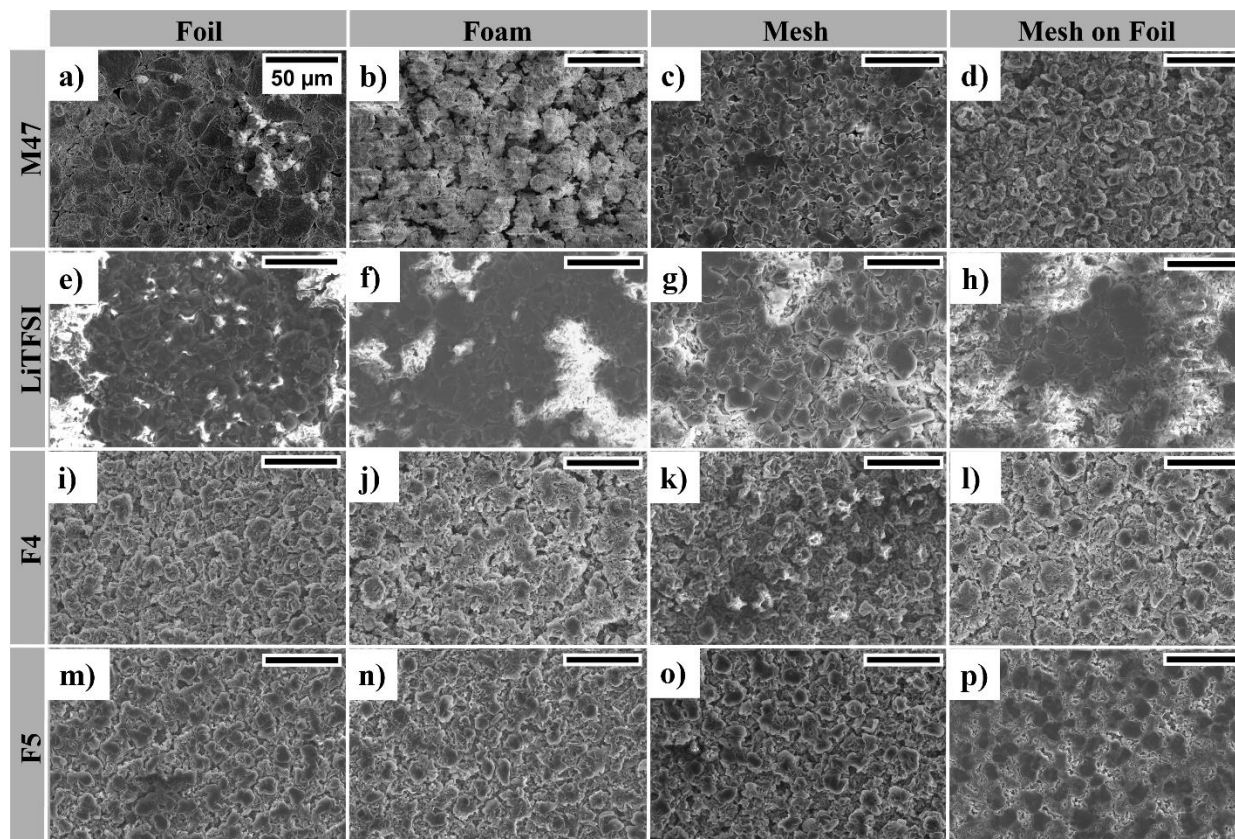


Figure 4-7: SEM images taken of the surface of the lithium of each current collector and electrolyte combination at the conclusion of shallow cycling utilizing M47 (a-d), LiTFSI (e-h), F4 (i-l), and F5 (m-p) electrolyte.

While surface imaging of cycled lithium may give some information and insight, differences in morphology and porosity are much more clearly observed in cross-sections of the material. Cross-sectional analysis was enabled by ion-milling in cryogenic conditions, revealing

greater differences between the combinations (Fig. 4-8). Overall, the current collectors in the LiTFSI electrolyte (Fig. 4-8e-h) exhibited the densest lithium, along with the foil and mesh in the M47 electrolyte (Fig. 4-8a and 4-8c) and the mesh on foil in F5 electrolyte (Fig. 4-8p). The F4 and F5 electrolytes consistently resulted in porous lithium (Fig. 4-8i-p), as well as the foam and mesh on foil in M47 electrolyte (Fig. 4-8b and 4-8d).

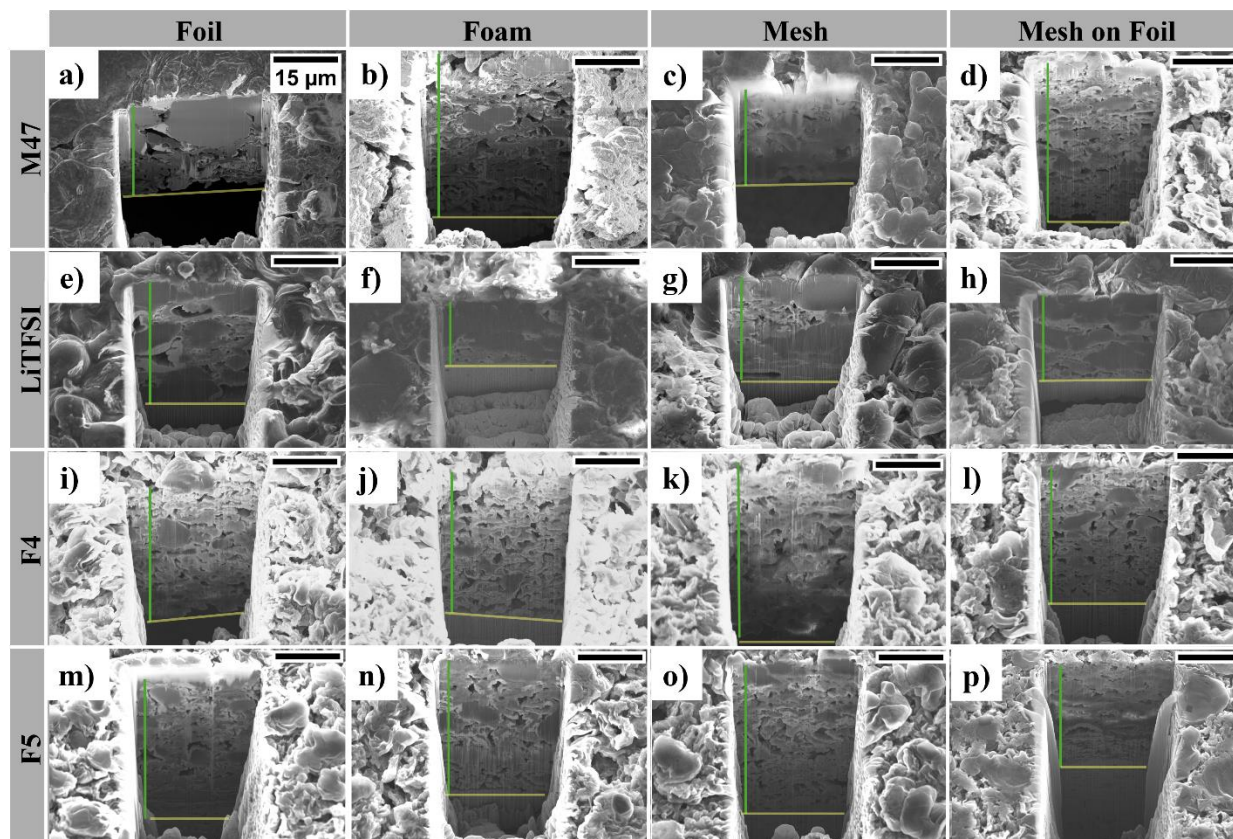


Figure 4-8: SEM images taken of the cross-section of the deposited lithium at the conclusion of shallow cycling. The foil, foam, mesh, and mesh on foil current collectors are respectively shown when cycled in M47 electrolyte (a-d), LiTFSI (e-h), F4 (i-l), and F5 (m-p) electrolyte. The yellow line marks the bottom of the deposited lithium, and the green bar emphasizes the thickness.

The cross-sectional analysis reveals a lack of similar morphologies when the same current collector is employed. However, fairly similar morphologies appear within each electrolyte group.

This observation again supports that electrolyte has the greater influence on lithium morphology and performance. Additionally, as with the polarization, no correlation between lithium morphology and CE is seen in this study. While the denser lithium of the LiTFSI cells correlates with high CEs, the similarly dense lithium in the M47 foil and mesh cells do not correspond to equal CEs. Conversely, the high porosity and thickness of the lithium in the F4 and F5 electrolyte do not lead them to have significantly lower CEs than the M47 cells.

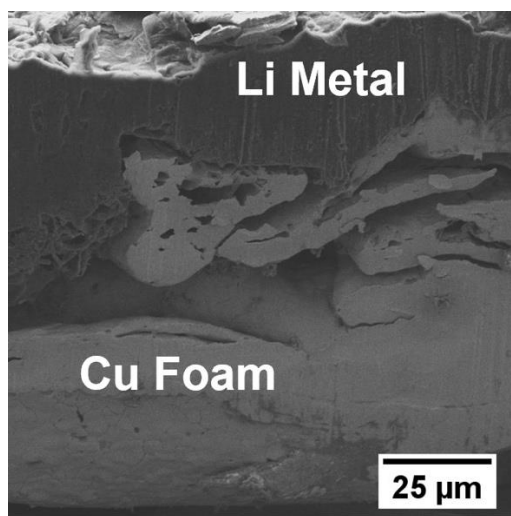


Figure 4-9: SEM cross sectional image of 10 mAh/cm² of lithium plated on copper foam in M47 electrolyte reveals that lithium does not penetrate into the structure of the foam but plates on the first surface directly facing the opposing electrode.

Contrary to many arguments for the use of 3D current collector structures, the increased surface area of the foam compared to the other current collectors does not consistently result in denser lithium plating in this study. Much of the theoretically beneficial area was unused as lithium was unable to penetrate the foam structure and plated directly on the first surface facing the opposing electrode (Fig. 4-9). Similarly, for the mesh and mesh on foil current collectors, lithium did not plate on the back side. A variety of techniques have been employed in literature to encourage lithium deposition within 3D structures, including applying an insulative coating on the

surface facing the opposite electrode and incorporating nanoparticles of lithophilic materials into the bulk of the current collector.^{19,61,121,123,145,155,191–193} However, these techniques inherently increase the inactive mass of the current collector which reduces overall energy density and their benefit when a lithium reservoir is present to begin has not been proven.

4.3.5. Outlook and Implications

Table 4-4: Areal densities in mg/cm² of current collectors investigated in this work.

Substrate	Foil	Foam	Mesh	Layered mesh on foil
Areal Density (mg/cm ²)	12.7	55.7	5	17.7

The lack of correlation between current collector structure and performance revealed in this study has interesting implications for the design of high energy density LMBs. A major barrier in increasing energy density in LMBs is the mass of inactive material, including current collectors. If the structure of the lithium anode current collector is inconsequential, manufacturers are able to select the lightest material without sacrificing performance. For the current collectors analyzed in this study, the copper mesh has the lowest density per unit area at 5 mg/cm² (Table 4-4). Compared to the foil with a density of 12.7 mg/cm², over half of the mass of the current collector can be eliminated with a simple material switch. Though there are other materials that could be used as current collectors, copper is still the principle material for anode current collectors due to its high conductivity and low manufacturing cost. The insights presented can have an immediate effect on high energy density cell manufacturing at large scale. Additionally, while this study only examined low current densities, mimicking C/10 cycling in a standard cell configuration, this insight is still valuable in design and proof-of-concept of LMBs pushing the boundaries on energy density. In the future, effort can be focused on electrolyte development to push CE closer to 100% without

spending time and money on intensive procedures to produce a particular current collector structure.

4.4. SUMMARY

In summary, four copper current collectors for lithium metal anodes were paired with four electrolytes to test the impact of 3D current collectors on LMB performance with a lithium reservoir present. No significant differences were observed when current collector varied and electrolyte was held constant. Conversely, significant differences in CE and the other metrics appeared when comparing the same current collector in different electrolytes. Thus, current collector selection, when copper is used as the base material, appears to be inconsequential in LMAs with a lithium reservoir while electrolyte formulation has significant effect on the anode performance. As such, current collector selection for high energy density LMBs is recommended to focus on mass to increase energy density. Energy should also be focused on the selection and design of electrolyte over current collector design.

Chapter 5. Conclusions and Outlook

The most relevant results of our work on 3D current collectors for lithium metal anodes have been described in this thesis. Specifically, investigations on the design of 3D current collectors guided by meta-analysis and machine learning and on 3D current collector performance compared to electrolyte impact when a lithium reservoir is present are presented in detail. As summaries can be found at the end of each chapter, the key results and insights of each chapter are noted below.

5.1. SUMMARY BY CHAPTER

5.1.1. *Summary of Chapter 1 – Introduction*

Chapter 1 outlined the background and motivation of this thesis. Battery operating principles, performance metrics, and key properties were discussed. An introduction to lithium metal batteries and the strategies pursued to stabilize them, including 3D current collectors, was also provided.

5.1.2. *Summary of Chapter 2 – 3D Current Collectors for Lithium Metal Anodes*

A discussion of the scientific principles behind the use of 3D current collectors for LMAs was detailed in Chapter 2. Among these are the concept of Sand's Time, electrode overpotential, volume expansion containment, and lithiophilicity. Key examples from literature were provided, and the gaps in knowledge this thesis seeks to fill were identified and described.

5.1.3. *Summary of Chapter 3 – Coupled Machine Learning and Meta-Analysis to Extract Key Properties of High-Performance 3D Current Collectors for Lithium Metal Batteries*

Based on the extensive literature on 3D current collectors for LMAs, a meta-analysis was undertaken to extract key properties of such structures that correlate to high performance. Some key highlights include:

- (1) Statistical and machine learning analysis were successfully employed to reveal correlation between high cycle life and CE in half cell testing for current collectors with a low to moderate specific surface area ($0.01\text{-}100\text{ m}^2/\text{g}$) and with the presence of oxygen and/or tin. Pore diameter was not shown to correlate strongly with performance apart from extremely small pores correlating with worse performance.
- (2) Experimental testing of copper foam- and carbon-based current collectors validated the conclusions drawn from the meta-analysis. The copper foam current collectors with oxygen and with tin consistently outperformed the plain copper foam, and the carbon fiber current collector with moderate specific surface area and pore diameter had a much greater cycle life and average CE than an activated carbon current collector with extremely high specific surface area and small pores.
- (3) The utility of meta-analysis coupled with statistics and machine learning for battery material design was demonstrated.

5.1.4. Summary of Chapter 4 – Deconvoluting the Impact of Current Collector Structure and Electrolyte Selection on Coulombic Efficiency of Lithium Metal Anodes

While the meta-analysis examined current collectors in an anode-free configuration, the impact of current collector structure on LMA performance under realistic conditions were examined in Chapter 4. Cycling performance was examined with the presence of a lithium reservoir on four current collectors and with the use of four standard and state-of-the-art electrolytes. Results revealed that:

- (1) Electrolyte selection has a significant impact on LMA performance, with significant differences in performance observed between configurations with the same current collector structure and varied electrolyte.

- (2) Current collector structure does not significantly impact LMA performance when electrolyte is held constant.
- (3) The greatest differences in polarization and impedance exist between cells with varied electrolyte, while cells with varied structure in the same electrolyte exhibit small differences that do not correlate to average CE measured.

5.2. OUTLOOK AND FUTURE DIRECTIONS

While significant progress has been made in stabilizing LMAs, shortfalls remain in their performance and safety. While 3D current collectors may be beneficial in anode-free configurations, realistic LMBs with a lithium reservoir were not shown to greatly benefit from them in this work. Nonetheless, numerous directions would still be beneficial to pursue, including:

- (1) Studying the impact of mechanical properties of 3D current collectors. To contain the volume expansion of lithium plating, a current collector must be able to handle the associated stresses, a factor that was not considered in the work here. If a current collector could be tailored to induce lithium deposition within its structure and then remain intact upon repeated cycling, the need for external pressure on LMBs may be eliminated, greatly increasing pack level energy density.
- (2) Expanding the scope of meta-analysis for 3D current collector design. The meta-analysis presented here was limited by available manpower and the time constraints of a PhD degree. Expanding the dataset to include data from additional published studies, as well as incorporating data from full cell testing could reveal additional insights.

In regard to the specific goal of greatly increasing energy density and performance of LMBs with a lithium reservoir on a cell level, it is likely that 3D current collectors are not a key solution to pursue. We recommend that work focus instead on:

- (1) Methods to further reduce copper foil mass, including investigating the limits of copper mesh. The copper mesh utilized in Chapter 4 provided over 50% reduction in mass compared to copper foil. The limits of how much material can be removed while still providing adequate electrical conductivity have not been investigated to our knowledge.
- (2) Development of lower density, high performing electrolytes. As demonstrated in Chapter 4, electrolyte selection has a significant impact on cell performance. By tuning electrolyte composition while also reducing the density, high performance can be enabled with less electrolyte mass.

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VITA

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